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CLAIMS

[Claim(s)]

[Claim 1] The optoelectric transducer characterized by installing this semi-conductor particle layer and the spacer layer which contains an insulating particle substantially between counter electrodes in the optoelectric transducer which has the semi-conductor particle layer, charge transfer layer, and counter electrode which adsorbed a conductive base material and the coloring matter painted on this.

[Claim 2] The light-transforming element of claim 1 by which said spacer layer is installed in the counter electrode side on a semi-conductor particle layer by unifying.

[Claim 3] The optoelectric transducer of claims 1 or 2 which said insulating particle becomes from the amorphous oxide containing at least one element chosen from silicon, boron, and Lynn, or an aluminum oxide.

[Claim 4] One optoelectric transducer of claims 1-3 whose mean particle diameter of said insulating particle is 5 or more-time 1000 or less times of the mean particle diameter of a semi-conductor particle.

[Claim 5] One optoelectric transducer of claims 1-4 in which said semi-conductor particle layer contains titanium oxide.

[Claim 6] One optoelectric transducer of claims 1-5 said whose coloring matter is metal complex coloring matter or poly methine coloring matter.

[Claim 7] The photoelectrochemical cell using one optoelectric transducer of claims 1-6.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optoelectric transducer and photoelectrochemical cell using the semi-conductor particle by which sensitization was carried out in detail with coloring matter about the photoelectrochemical cell which used an optoelectric transducer and this.

[0002]

[Description of the Prior Art] Although compound solar batteries, such as a single crystal silicon solar cell, a polycrystal silicon solar cell, an amorphous-silicon solar cell, a cadmium telluride, and selenium-ized indium copper, are set as the object of utilization or the main researches and developments, when making it spread, as for photovoltaics, a manufacturing cost, raw-material reservation, and an energy pay back time need to conquer troubles, such as being long. On the other hand, although many solar batteries using the organic material which pointed to large-area-izing or low-pricing were also proposed until now, conversion efficiency was low and there was a problem that endurance was also bad.

[0003] The ingredient and manufacturing technology for creating the optoelectric transducer and solar battery using the semi-conductor particle by which sensitization was carried out to Nature (the 353rd volume, the 737-740th page, 1991), a U.S. Pat. No. 4927721 number, etc. with coloring matter, and this in such a situation were indicated. The proposed cell is a wet solar battery which uses as a working electrode the titanium-dioxide porosity thin film by which spectral sensitization was carried out with the ruthenium complex. The first advantage of this method is a point that a cheap optoelectric transducer can be offered since it can use without refining cheap oxide semiconductors, such as a titanium dioxide, to a high grade, and since broadcloth [the second advantage / absorption of the coloring matter used], it is that the light of almost all the wavelength fields of a visible ray is convertible for the electrical and electric equipment.

[0004] However, in order to have put in practical use as a solar battery, the improvement in the endurance of a charge transfer layer was an important technical problem. Although the organic solvent solution of a redox compound was used as a charge transfer layer in an early examination, scattering of an organic solvent occurred in these components, and there was a problem that degradation of the engine performance is large. As an approach of solving this, although use of use of the solvent of a high-boiling point and low-temperature fused salt, and a solid-state-like charge transportation ingredient had been considered, since it was in the inclination for migration of a charge to become slow, it was required to make thickness of a layer thin in these charge transfer layers.

[0005] It was common to have prevented the short circuit by the direct contact to the oxide-semiconductor layer and counter electrode used as a negative electrode by putting through a spacer between the base material which supported the semi-conductor particle with the conventional component, and the base material which supported the counter electrode.

[0006] However, by the approach by the spacer, in order to make thickness of a charge transfer layer thin, when it was going to narrow inter-electrode distance, the problem that the short circuit by direct contact of an electrode often occurred by fluctuation of the thickness of a semi-conductor particle layer and fluctuation of spacer thickness occurred.

[0007] Although the charge transfer layer itself functioned as a spacer layer when a charge transfer layer was a solid-state, it was difficult to obtain the engine performance which a partial short circuit may take place and was too stabilized with the detailed irregularity of a semiconductor electrode or a counter electrode even in this case.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the optoelectric transducer and photoelectrochemical cell which prevented the short circuit inside a component, without degrading the engine performance of photo electric conversion.

[0009]

[Means for Solving the Problem] The technical problem of this invention was attained by the matter of the following which specifies this invention, and its desirable mode.

(1) The optoelectric transducer characterized by installing this semi-conductor particle layer and the spacer layer which contains an insulating particle substantially between counter electrodes in the optoelectric transducer which has the semi-conductor particle layer, charge transfer layer, and counter electrode which adsorbed a conductive base material and the coloring matter painted on this.

(2) The light-transforming element of the above (1) by which said spacer layer is installed in the counter electrode side on a semi-conductor particle layer by unifying.

(3) The above (1) which said insulating particle becomes from the amorphous oxide containing at least one element chosen from silicon, boron, and Lynn, or an aluminum oxide, or (2) optoelectric transducers.

(4) said -- insulation -- a particle -- mean particle diameter -- a semi-conductor -- a particle -- mean particle diameter -- five -- a time -- more than -- 1000 -- a time -- less than -- it is -- the above -- (-- one --) - (-- three --) -- either -- an optoelectric transducer .

(5) said -- insulation -- a particle -- mean particle diameter -- a semi-conductor -- a particle -- mean particle diameter -- five -- a time -- more than -- 100 -- a time -- less than -- it is -- the above -- (-- one --) - (-- four --) -- either -- an optoelectric transducer .

(6) One optoelectric transducer of above-mentioned (1) - (5) in which said semi-conductor particle layer contains titanium oxide.

(7) One optoelectric transducer of above-mentioned (1) - (6) said whose coloring matter is metal complex coloring matter or poly methine coloring matter.

(8) The above (1) Photoelectrochemical cell using one optoelectric transducer of - (7).

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. First, the configuration and ingredient of the optoelectric transducer of this invention and a photoelectrochemical cell are explained in full detail. The optoelectric transducer which carried out coloring matter sensitization in this invention consists of the semi-conductor film (sensitization layer), charge transfer layer, and counter electrode which carried out sensitization with the coloring matter installed on a conductive base material and a conductive base material. Here, the thing which enabled it to use this optoelectric transducer for the cell application made to work in an external circuit is called a photoelectrochemical cell. A sensitization layer may be designed according to the purpose and a monolayer configuration or a multilayer configuration is sufficient as it. The light which carried out incidence to the sensitization layer excites coloring matter etc. The excited coloring matter has the high electron of energy, and this electron is passed to the conduction band of a semi-conductor particle from coloring matter etc., and it reaches a conductive base material by diffusion further. At this time, molecules, such as coloring matter, serve as an oxidant. While the electron on a conductive base material works in a photoelectrochemical cell in an external circuit, return, coloring matter, etc. are reproduced to oxidants, such as coloring matter, through a counter electrode and a charge transfer layer. The semi-conductor film works as a negative electrode of this cell. In addition, in this invention, the constituents of each class may be diffusing and mixing mutually on the boundary of each layer (for example, the boundary of the conductive layer of a conductive base material, and a sensitization layer, the boundary of a sensitization layer and a charge transfer layer, the boundary of a charge transfer layer and a counter electrode, etc.). However, the semi-conductor film and a counter electrode must not touch directly.

[0011] This invention is characterized by installing among both the spacer layer which consists of an insulating particle substantially, in order to prevent the above-mentioned semi-conductor film and the short circuit of a counter electrode. As a particle of electric insulation, electrical conductivity is the matter below 10-3 Siemens / cm substantially [this invention], and to the electrolytic solution, if it is the inactive matter, the thing of arbitration will be used. Oxide glass or a crystalline oxide is mentioned as such matter. The example of the desirable oxide glass matter is oxide glass containing a kind of element chosen from silicon, boron, and Lynn at least. Moreover, an aluminum oxide is mentioned as an example of a desirable crystalline oxide.

[0012] Still more desirable oxide glass is glass of a presentation with which softening temperature becomes 700 or less degrees including one of silicon, boron, and the Lynn at least. For example, although the following presentations are mentioned, this invention is not limited to this.

[0013]

$Na_0.2B_0.4P_0.4OxRb_0.2B_0.4P_0.4OxPb_0.5B_0.25Si_0.25OxSn_0.2Pb_0.1P_0.5F_0.2OxPb_0.2Zn_0.1B_0.7OXTl_0.1Pb_0.2B_0.7Ox$

[0014] Oxide glass is obtained by mixing and fusing the oxide of a configuration raw material. The obtained glass is made into predetermined size with the grinder and classifier which were known well, and is used. As a grinder, a vibration ball mill and a revolution type jet mill are used, and a vibration screen and a pneumatic elutriation machine are used as a classifier.

[0015] The thing of one 5 to 1000 times the particle diameter of the semi-conductor particle which acts as an electrode of this is used, and the above-mentioned electric insulation particle is 100 times from 5 times preferably.

[0016] In this invention, with the semi-conductor by which coloring matter sensitization was carried out, generating of light absorption, the electron by this, and an electron hole takes place mainly in coloring matter, and a semi-conductor bears reception and the role to transmit for this electron.

[0017] The compound which has the so-called compound semiconductor or so-called perovskite structure represented by the metal chalcogenides (for example, oxide, a sulfide, a selenide, etc.) other than an element semiconductor like silicon and germanium as a semi-conductor can be used. The oxide of titanium, tin, zinc, iron, a tungsten, a zirconium, a hafnium, strontium, an indium, a cerium, an yttrium, a lanthanum, vanadium, niobium, or a tantalum, cadmium, zinc, lead, silver, antimony, the sulfide of a bismuth, cadmium, a leaden selenide, the telluride of cadmium, etc. are mentioned preferably as metal chalcogenide. As other compound semiconductors, phosphides, such as zinc, a gallium, an indium, and cadmium, a gallium arsenide, a copper-indium-selenide, a copper-indium-sulfide, etc. are mentioned.

[0018] Moreover, strontium titanate, titanic-acid calcium, titanic-acid sodium, barium titanate, and a niobic acid potassium are mentioned preferably as a compound which has a perovskite structure.

[0019] Si, TiO₂, SnO₂, Fe 2O₃, WO₃, ZnO and Nb 2O₅, CdS, ZnS and PbS, Bi₂S₃, CdSe, CdTe, GaP and InP, GaAs, and CuInS₂ and CuInSe₂ are specifically more preferably mentioned as a semi-conductor used for this invention. It is TiO₂, ZnO, SnO₂, Fe 2O₃, WO₃ and Nb 2O₅, CdS and PbS, CdSe, InP, GaAs, and CuInS₂ and CuInSe₂ still more preferably, is TiO₂ or Nb 2O₅ especially preferably, and is TiO₂ most preferably.

[0020] A single crystal or polycrystal is sufficient as the semi-conductor used for this invention. Although a single crystal is desirable as conversion efficiency, in respect of a manufacturing cost, raw-material reservation, an energy pay back time, etc., polycrystal is desirable, and the particle semi-conductor of micrometer size is especially desirable from NANOMETORU.

[0021] As for the particle size of these semi-conductor particles, it is desirable that it is 5-200nm as a primary particle in the mean particle diameter using the diameter when converting projected area into a circle, and it is especially desirable that it is 8-100nm. Moreover, it is desirable that it is 0.01-100 micrometers as mean particle diameter of the semi-conductor particle in a distributed object (aggregated particle).

[0022] Moreover, the particle from which two or more kinds of grain-size distribution differs may be mixed and used, and it is desirable that the average size of a small particle is 5nm or less in this case. Moreover, grain size is big in order to scatter incident light and to raise the rate of optical capture, for example, an about 300nm semi-conductor particle may be mixed.

[0023] the method of producing a semi-conductor particle -- a sol-gel method given in "thin-layer-coating technique by the sol-gel method" (1995) etc. of Sumio Sakuhana's company (1988) of the "science of sol-gel method" AGUNE ** style, and a technical-information association, and Tadao Sugimoto -- "new synthesis method GERUZORU -- composition of the monodisperse particle by law, and size gestalt control" wait -- ****, the 35th volume, and No. 9 GERUZORU given in 1018 page (1996) from 1012 pages -- law is desirable. Moreover, the approach of producing an oxide for the chloride which Degussa developed by elevated-temperature hydrolysis in an oxyhydrogen flame is also desirable.

[0024] moreover, the sol-gel method of the above [the case of titanium oxide] and GERUZORU -- although each elevated-temperature hydrolyzing method is desirable in an oxyhydrogen flame in law and a chloride, the sulfuric-acid method of a publication and a chlorine method can also be further used for "titanium oxide physical-properties and applied-technology" Gihodo Shuppan (1997) of the Seino study.

[0025] the inside of the sol-gel method of the above [the case of titanium oxide] -- especially -- a varve etc. -- " -- journal OBU American ceramic society [] -- a thing, a barn side, etc. given [the 80th volume, No. 12, and 3157 pages to] in 3171 page (1997) " -- " chemical MATERIARUZU [] -- an approach given [volume / 10th / No. 9 and 2419 pages to] in 2425 page" is desirable.

[0026] Or a conductive base material will not have conductivity in the base material itself like a metal, it can use the base material of the glass which has a conductive layer (electric conduction agent layer) containing an electric conduction agent, or plastics for a front face. In the case of the latter, as a desirable electric conduction agent, a metal, carbon (for example, platinum, gold, silver, copper, aluminum, a rhodium, an indium, etc.), or conductive metallic oxides (what doped the fluorine to an indium-tin multiple oxide and the tin oxide) are mentioned. As for the thickness of the above-mentioned electric conduction agent layer, it is desirable that it is about 0.02-10 micrometers.

[0027] A conductive base material is so good that surface electrical resistance is low. As range of desirable surface electrical resistance, it is below 100ohms / **, and they are below 40ohms / ** still more preferably. Although there is especially no limit in this minimum, they are usually 0.1ohms / ** extent.

[0028] The substantially transparent thing of a conductive base material is desirable. It means that the permeability of light is 10% or more substantially as it is transparent, it is desirable that it is 50% or more, and especially 70% or more is desirable. What painted the conductive metallic oxide on glass or plastics as a transparent conductive base material is desirable. Especially the electrically conductive glass that deposited the conductive layer which consists of diacid-ized tin which doped the fluorine also in this on the transparency substrate made with the soda lime float glass of low cost is desirable. Moreover, it is good to use for a flexible optoelectric transducer or a flexible solar battery what prepared the above-mentioned conductive layer in the transparency polymer film by low cost. There is tetra-acetyl-cellulose (TAC), polyethylene terephthalate (PET), polyethylenenaphthalate (PEN), SHINJIKUTA tic poly sterene (SPS), polyphenylene sulfide (PPS), polycarbonate (PC), polyacrylate (PAr), polysulfone (PSF), polyester sulfone (PES), polyether imide (PEI), annular polyolefine, and bromine-ized phenoxy etc. in a transparency polymer film. When using a transparent conductive base material, as for light, it is desirable to carry out incidence from the base material side. In this case, as for the coverage of conductive metallic oxide, per [0.01-100g] two are [1m of base materials of glass or plastics] desirable.

[0029] It is desirable to use a metal lead in order to lower resistance of a transparent conductive substrate. The quality of the material of a metal lead has desirable metals, such as aluminum, copper, silver, gold, platinum, and nickel, and is desirable. [of especially aluminum and silver] It is desirable to install a metal lead in a transparency substrate in vacuum evaporationo, a SUPPATA ring, etc., and to prepare on it the tin oxide which doped the fluorine, or the transparency conductive layer which consists of ITO film. Moreover, after preparing the above-mentioned transparency conductive layer in a transparency substrate, it is also desirable to install a metal lead on a transparency conductive layer. The fall of the amount of incident light by metal lead installation is 1 - 5% more preferably 1 to 10%.

[0030] As an approach of painting a semi-conductor particle on a conductive base material, the approach of applying the dispersion liquid or the colloidal solution of a semi-conductor particle on a conductive base material, the above-mentioned sol-gel method, etc. are mentioned. When fertilization of an optoelectric transducer, and liquid nature and the versatility of a base material are considered, a wet film grant method is comparatively advantageous. As a wet film grant method, the applying method and print processes are typical.

[0031] In case the approach of distributing while grinding using the approach and mill which are mashed with a mortar besides the above-mentioned sol-gel method as an approach of creating the dispersion liquid of a semi-conductor particle, or a semi-conductor is compounded, the approach of depositing as a particle and using it as it is in a solvent, etc. is mentioned. As a dispersion medium, water or various kinds of organic solvents (for example, a methanol, ethanol, isopropyl alcohol, dichloromethane, an acetone, an acetonitrile, ethyl acetate, etc.) are mentioned. A polymer, a surfactant, an acid, or a chelating agent may be used as a distributed assistant if needed in the case of distribution.

[0032] As the method of application, the slide hopper method given in application and the wire bar methods currently indicated by JP,58-4589,B as what can do a meter ring in the same part, such as the Ayr knife method and the blade method, a U.S. Pat. No. 2681294 number, said 2761419 numbers, said 2761791 numbers, etc., the extrusion method, the curtain method, etc. are desirable as a roller, a dip method, and a meter ring system as an application system. Moreover, the spin method and a spray method are also preferably used as a general aviation.

[0033] As the wet printing approach, letterpress, offset, and the three major print processes of gravure are begun from the former, and an intaglio, the rubber version, screen-stencil, etc. are desirable.

[0034] A desirable film grant method is chosen with liquid viscosity or wet thickness from said approaches.

[0035] Liquid viscosity is greatly influenced with additives, such as a class of semi-conductor particle, dispersibility and a use solvent kind, a surface active agent, and a binder. In a viscous liquid (for example, 0.01 - 500Poise), the extrusion method and the cast method are desirable and it is possible for the slide hopper method, the wire bar method, or the spin method to be desirable, and to make it the uniform film with hypoviscosity liquid (for example, 0.1 or less Poises).

[0036] in addition, a certain amount of [in the case of spreading of the hypoviscosity liquid by the extrusion method / coverage] amount -- that -- ***** is possible.

[0037] Moreover, screen-stencil is often used for painting of the hyperviscous paste of a semi-conductor particle, and this technique can also be used.

[0038] Thus, what is necessary is just to choose the grant method of the wet film suitably corresponding to parameters, such as liquid viscosity of coating liquid, coverage, a base material, and a spreading rate.

[0039] Furthermore, it is not necessary to limit a semi-conductor particle content layer with a monolayer. It is also possible to carry out multilayer spreading of the dispersion liquid from which the particle size of a particle is different, and the classes of semi-conductor differ, or multilayer spreading of the spreading layer from which the presentation of a binder and an additive differs can also be carried out, and also when thickness is insufficient, multilayer spreading is effective at one-time spreading. The extrusion method or the slide hopper method is suitable for multilayer spreading.

Moreover, when carrying out multilayer spreading, a multilayer may be applied to coincidence, and sequential two coats may be carried out about ten times from several times. If it is furthermore sequential two coats, screen printing can also be used preferably.

[0040] Since the amount of support coloring matter per unit projected area generally increases so that the thickness of a semi-conductor particle content layer increases, the rate of capture of light becomes high, but since the diffusion length of the generated electron increases, the loss by charge recombination also becomes large. Therefore, although desirable thickness exists in a semi-conductor particle content layer, it is 0.1-100 micrometers typically. When using as a photoelectrochemical cell, it is desirable that it is 1-30 micrometers, and it is more desirable that it is 2-25 micrometers. The coverage per two has [1m of base materials of a semi-conductor particle] 5-desirable 100g to 0.5-400g, and a pan.

[0041] As for a semi-conductor particle, it is desirable to heat-treat in order to contact particles electronically after applying to a conductive base material, and in order to raise improvement in paint film reinforcement and adhesion with a base material. The range of desirable heat-treatment temperature is 40 degrees C or more less than 700 degrees C, and is 100 degrees C or more 600 degrees C or less more preferably. Moreover, the heating processing time is 10 minutes - about 10 hours. When using low base materials of the melting point or softening temperature, such as a polymer film, high temperature processing is not desirable in order to cause degradation of a base material. Moreover, it is desirable that it is low temperature as much as possible also from the viewpoint of cost. Low-temperature-izing is possible by concomitant use of the small semi-conductor particle 5nm or less described previously, the heat-treatment under existence of a mineral acid, etc.

[0042] Moreover, it is the purpose which the surface area of a semi-conductor particle is increased, or raises the purity near the semi-conductor particle after heat-treatment, and raises the electron injection effectiveness from coloring matter to a semi-conductor particle, for example, electrochemical plating processing using chemical plating and the titanium-trichloride water solution using a titanium-tetrachloride water solution may be performed.

[0043] As for a semi-conductor particle, what has large surface area is desirable so that much coloring matter can be adsorbed. For this reason, as for the surface area in the condition of having painted the semi-conductor particle layer on the base material, it is desirable that they are 10 or more times to projected area, and it is desirable that they are further 100 or more times. Although there is especially no limit in this upper limit, they are usually about 1000 times.

[0044] As for the spacer layer of this invention, it is desirable to install on the above-mentioned semi-conductor particle layer (namely, being a counter electrode side a base material and the opposite side). Installation of a spacer layer is the same approach as painting of the above-mentioned semi-conductor particle, and can be installed on a semi-conductor particle layer. As for a spacer layer, it is desirable to do in this way and to unite with a semi-conductor particle layer. Although before heat-treatment of the above-mentioned semi-conductor particle layer or the back is available for installation of a spacer layer, heat-treating after spacer layer installation is desirable.

[0045] The coloring matter used for this invention has metal complex coloring matter or desirable methine coloring matter. Since the wavelength region of photo electric conversion is made large as much as possible and conversion efficiency is raised in this invention, two or more kinds of coloring matter is mixable. And the coloring matter mixed so that it may double with the target wavelength region and intensity distribution of the light source, and its rate can be chosen. As for such coloring matter, it is desirable to have the suitable joint radical (interlocking group) to the front face of a semi-conductor particle. The chelation radical which has pi conductivity like a COOH radical, SO₃H set, a cyano group, -P(O)(OH)₂ set, -OP(O)(OH)₂ set or an oxime, dioxime, hydroxyquinoline, salicylate, and alpha-KETOENO rate as a desirable joint radical is mentioned. Also in this, a COOH radical, -P(O)(OH)₂ set, and especially -OP(O)(OH)₂ set are desirable. These radicals may form alkali metal etc. and a salt, and may form inner salt.

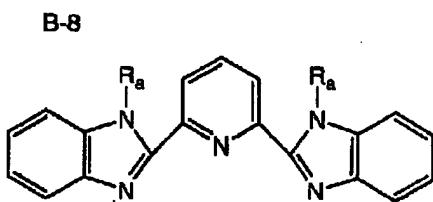
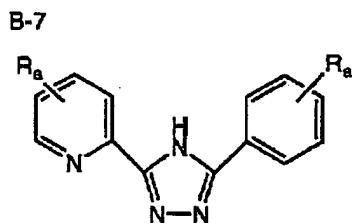
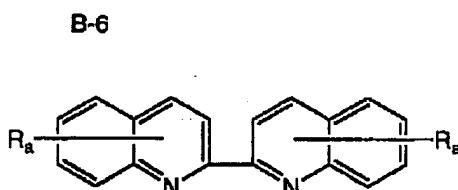
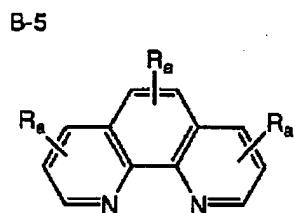
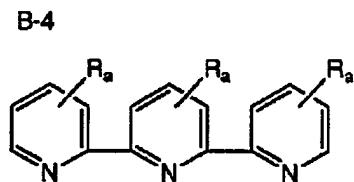
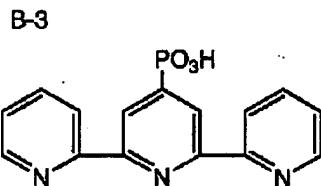
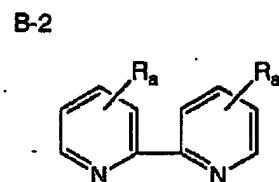
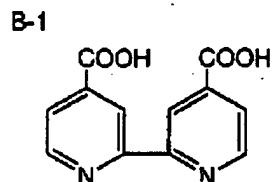
Moreover, if an acidic group is contained like [in case a methine chain forms a squarylium ring and a crocodile NIUMU ring] in the case of poly methine coloring matter, it will be good also considering this part as a joint radical.

[0046] The coloring matter preferably used for below by this invention is explained concretely. When the coloring matter used for this invention is metal complex coloring matter, ruthenium complex coloring matter is desirable and the coloring matter further expressed with the following formula (I) is desirable.

Formula (I) (A1) Among a pRuBaBbBc type (I), p is 0-2 and is 2 preferably. Ru expresses a ruthenium. A1 is a ligand chosen from Cl, SCN, H₂O, Br, I, CN and NCO, and SeCN. Ba, Bb, and Bc are organic ligands independently chosen from B-1 to B-8 of the following, respectively.

[0047]

[Formula 1]



[0048] Here, Ra expresses the aralkyl radical which is not permuted [a permutation or] with the alkyl group which is not permuted [a permutation or] and 7-12 C numbers, and expresses with a hydrogen atom, a halogen atom, and 1-12 carbon atomic numbers (henceforth C number) the aryl group which is not permuted [a permutation or] by 6-12 C numbers. The alkyl parts of the above-mentioned alkyl group and an aralkyl radical may be straight chains-like, or may be the letters of branching, and the aryl parts of an aryl group and an aralkyl radical may be monocycles, or may be polycyclic (the condensed ring, ring set).

[0049] as the ruthenium complex coloring matter used for this invention -- for example, a U.S. Pat. No. 4927721 number -- said -- No. 4684537 -- said -- No. 5084365 -- said -- No. 5350644 -- said -- No. 5463057 -- said -- the complex coloring matter of a publication is mentioned in No. 5525440 and a JP,7-249790,A specification.

[0050] Although the desirable example of the metal complex coloring matter used for this invention is shown below, this invention is not limited to these. The coloring matter E, H, and K of example use is also mentioned.

〔0051〕

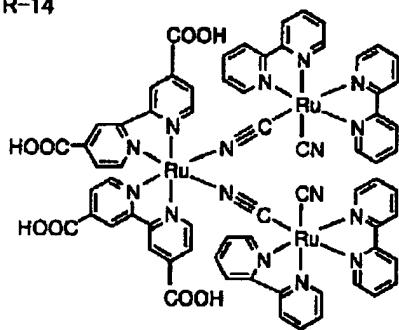
[Formula 2]

| No. | A ₁ | p | B _a | B _b | B _c | R ₄ |
|------|----------------|---|----------------|----------------|----------------|----------------|
| R-1 | SCN | 2 | B-1 | B-1 | — | — |
| R-2 | CN | 2 | B-1 | B-1 | — | — |
| R-3 | Cl | 2 | B-1 | B-1 | — | — |
| R-4 | Br | 2 | B-1 | B-1 | — | — |
| R-5 | I | 2 | B-1 | B-1 | — | — |
| R-6 | SCN | 2 | B-1 | B-2 | — | H |
| R-7 | SCN | 1 | B-1 | B-3 | — | — |
| R-8 | Cl | 1 | B-1 | B-4 | — | H |
| R-9 | I | 2 | B-1 | B-5 | — | H |
| R-10 | SCN | 2 | B-1 | B-6 | — | H |
| R-11 | CN | 2 | B-1 | B-7 | — | H |
| R-12 | Cl | 1 | B-1 | B-8 | — | H |
| R-13 | — | 0 | B-1 | B-1 | — | — |

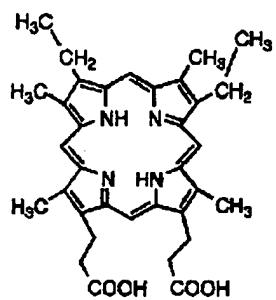
[0052]

[Formula 3]

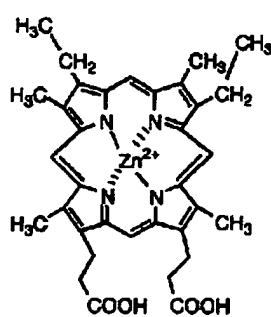
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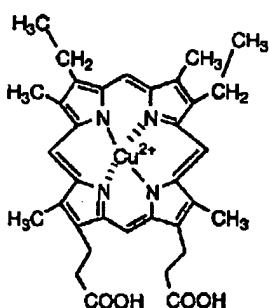
R-15



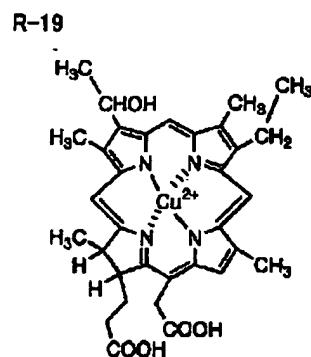
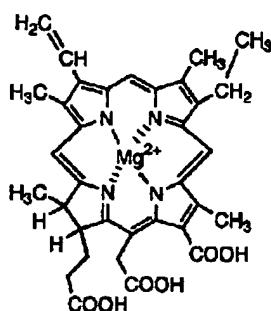
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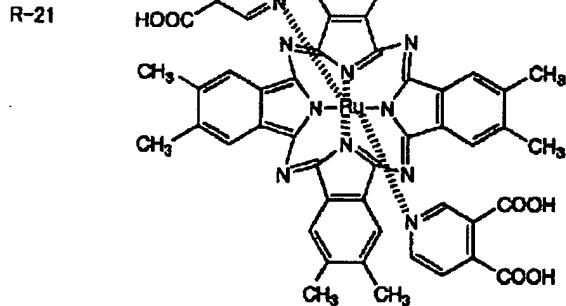
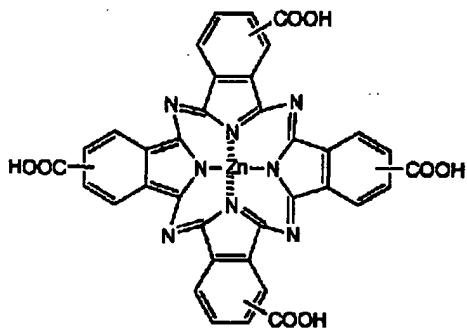
R-17



[0053]
[Formula 4]
R-18



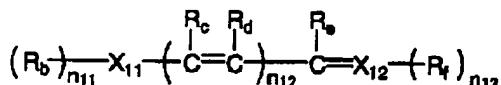
R-20



[0054] When the coloring matter used for this invention is methine coloring matter, the coloring matter expressed with the formula (II) explained below, a formula (III), a formula (IV), or a formula (V) is desirable.

[0055]

[Formula 5]
式(II)

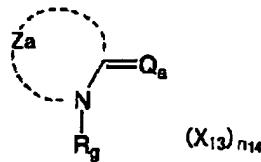


[0056] Rb and Rf express a hydrogen atom, an alkyl group, an aryl group, or a heterocycle radical respectively among a formula, and Rc-Re expresses a hydrogen atom or a substituent respectively. It may join together mutually and Rb-Rf may form a ring. X11 and X12 express nitrogen, oxygen, sulfur, a selenium, and a tellurium respectively. n11 and n13 express the integer of 0-2 respectively, and n12 expresses the integer of 1-6. The compound expressed with a formula (II) may have a counter ion according to the charge of the whole molecule.

[0057] The alkyl group in the above, the aryl group, and the heterocycle radical may have the substituent. An alkyl group may be a straight chain, or may be branched chain, and, as for an aryl group and a heterocycle radical, a monocycle may also be polycyclic (the condensed ring, ring set). Moreover, the ring formed of Rb-Rf may have the substituent, and may be a monocycle, or may be the condensed ring.

[0058]
[Formula 6]

式(III)



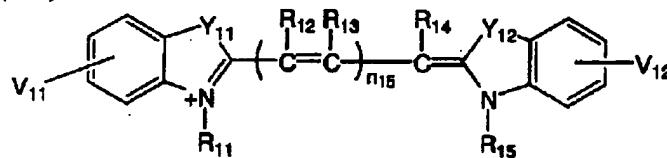
[0059] Za expresses a nonmetal atom group required to form nitrogen-containing heterocycle among a formula. Rg is an alkyl group or an aryl group. Qa expresses a methine group required for the compound expressed with a formula (III) to form methine coloring matter, or the Pori methine group. X₁₃ expresses a charge equilibrium counter ion, and n₁₄ expresses or more 0 ten or less number required to neutralize the charge of a molecule.

[0060] The nitrogen-containing heterocycle formed by above Za may have the substituent, and may be a monocycle, or may be the condensed ring. Moreover, the alkyl group and the aryl group may have the substituent, an alkyl group may be a straight chain or may be branched chain, and an aryl group may be a monocycle or may be polycyclic (the condensed ring, ring set).

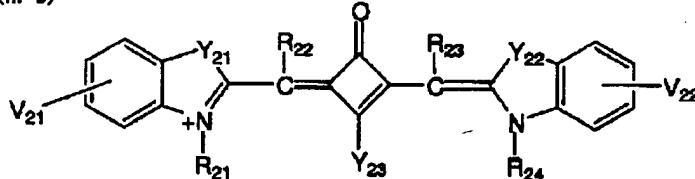
[0061] As for the coloring matter expressed with a formula (III), it is desirable that it is coloring matter expressed with following type (III-a) - (III-d).

[0062]

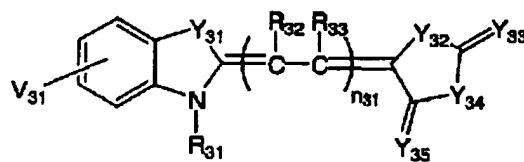
[Formula 7]
(III-a)



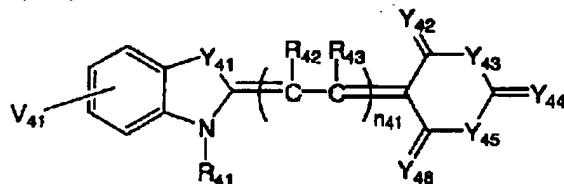
(III-b)



(III-c)



(III-d)



[0063] R11-R15, R21-R24, R31-R33, and R41-R43 express a hydrogen atom, an alkyl group, an aryl group, or a heterocycle radical independently among formula (III-a) - (III-d), respectively, and Y11, Y12, Y21, Y22, Y31-Y35, and Y41-Y46 express oxygen, sulfur, a selenium, a tellurium, -CR₁₆R₁₇-, or -NR₁₈- independently, respectively. R16-R18 express a hydrogen atom, an alkyl group, an aryl group, or a heterocycle radical independently, respectively. Y23 expresses O-, S-, Se-, Te-, or -NR₁₈-.

[0064] V11, V12, V21, V22, V31, and V41 express a substituent independently, respectively, and n₁₅, n₃₁, and n₄₁ express the integer of 1-6 independently, respectively. The compound expressed with formula (III-a) - (III-d) may have the counter ion according to the charge of the whole molecule.

[0065] The alkyl group in the above, the aryl group, and the heterocycle radical may have the substituent, an alkyl group may be a straight chain or may be branched chain, and an aryl group and a heterocycle radical may be

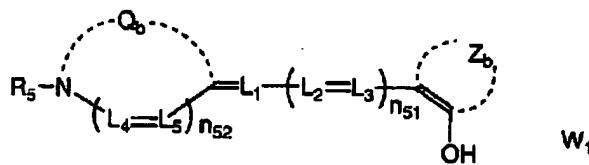
monocycles, or may be polycyclic (the condensed ring, ring set).

[0066] The example of the above poly methine coloring matter is indicated in detail by the M.Okawara, T.Kitao, T.Hirasima, and M.Matuoka work Organic Colorants (Elsevier) etc.

[0067]

[Formula 8]

式 (I V)



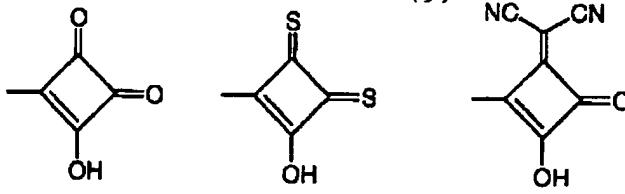
[0068] An atomic group required in order that Qb may complete the nitrogen-containing heterocycle of 5 members or 6 members may be expressed among a formula (IV), and Qb may be condensing the ring, and you may have the substituent. As a desirable example of the heterocycle completed by Qb Although a benzothiazole nucleus, a benzo oxazole nucleus, benzoselenazole nucleus, a benzotellurazole nucleus, 2-quinoline nucleus, 4-quinoline nucleus, a benzimidazole nucleus, a thiazoline nucleus, an India renin nucleus, an OKISA diazole nucleus, a thiazole nucleus, and an imidazole nucleus are mentioned Still more preferably A benzothiazole nucleus, a benzo oxazole nucleus, a benzimidazole nucleus, It is benzoselenazole nucleus, 2-quinoline nucleus, 4-quinoline nucleus, and an India renin nucleus, and they are a benzothiazole nucleus, a benzo oxazole nucleus, 2-quinoline nucleus, 4-quinoline nucleus, and an India renin nucleus especially preferably. As a substituent on a ring, a carboxylic-acid radical, a phosphonic acid radical, a sulfonic group, a halogen atom (F, Cl, Br, I), a cyano group, and an alkoxy group (methoxy --) Aryloxy radicals, such as ethoxy ** methoxyethoxy (phenoxy etc.), an alkyl group (methyl, ethyl, cyclo propyl, and cyclo -- KISHIRU and trifluoromethyl --) Alkylthio groups (a methylthio, ethyl thio, etc.), such as methoxy ethyl, an allyl compound, and benzyl, alkenyl radicals (vinyl, 1-propenyl, etc.), an aryl group, or heterocycle radicals (phenyl, thiienyl, toluyl one, chlorophenyl, etc.) are mentioned.

[0069] Zb expresses an atomic group required in order to complete 3 thru/or 9 membered-rings constituted with the atom chosen from a carbon atom, an oxygen atom, a nitrogen atom, a sulfur atom, and a hydrogen atom. Preferably as a ring completed by Zb, it is the ring in which a frame is formed, is expressed with following more desirable (a) - (e) by 4 thru/or six carbon, and is (a) most preferably.

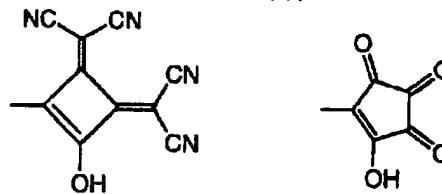
[0070]

[Formula 9]

(ア)



(エ)



[0071] L1, L2, L3, L4, and L5 express the methine group which may have the substituent independently, respectively. As a substituent, it is the alkyl group (it is the thing of 1 thru/or 7 preferably [it is desirable and] to the carbon atomic number 1 thru/or 12, and a pan) which is not permuted [a permutation or]. For example, methyl, ethyl, propyl, isopropyl, cyclo propyl, The aryl group which is not permuted [permutations, such as butyl, 2-carboxy ethyl, and benzyl, or] (it is the thing of 6 thru/or 8 preferably [it is desirable and] to the carbon atomic number 6 thru/or 10, and a pan) For example, phenyl, toluyl one, chlorophenyl, o-carboxyphenyl, A heterocycle radical (for example, pyridyl, thiienyl, furanyl, pyridyl, barbituric acid), a halogen atom (for example, chlorine, a bromine) and an alkoxy group (for example, methoxy --) Ethoxy, the amino group (preferably the carbon atomic number 1 thru/or 12, being the thing of 6

thru/or 12 still more preferably for example, diphenylamino, methylphenylamino, and 4-acetyl piperazine-1-IRU), an oxo-radical, etc. are mentioned. The substituent on these methine groups can be connected mutually, and may form rings, such as a cyclopentene ring, a cyclohexene ring, and a squarylium ring, or can also form an auxochrome and a ring.

[0072] n51 expresses the integers from 0 to 4, and is 0 to 3 preferably. n52 is 0 or 1.

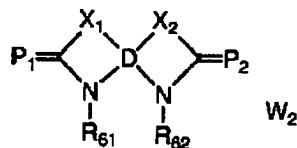
[0073] R5 expresses a substituent. It is the aliphatic series radical which may have the aromatic series radical or substituent which may have a substituent preferably as a substituent, and the carbon atomic numbers of an aromatic series radical are 5 thru/or 6 preferably [it is desirable and] to 1 thru/or 16, and a pan. The carbon atomic numbers of an aliphatic series radical are 1 thru/or 6 preferably [it is desirable and] to 1 thru/or 10, and a pan. As non-permuted an aliphatic series radical and an aromatic series radical, a methyl group, an ethyl group, n-propyl group, n-butyl, a phenyl group, a naphthyl group, etc. are mentioned.

[0074] A counter ion when a counter ion is required is expressed to W1 neutralizing a charge. A certain coloring matter is a cation and an anion, or it is dependent on the auxochrome and substituent whether it has net ionic charge. When a substituent has a dissociative radical, it may dissociate, you may have a negative charge and the charge of the whole molecule is neutralized by W1 also in this case. ammonium ion (for example, tetra-alkylammonium ion --) inorganic in a typical cation, or organic It may be pyridinium ion and alkali-metal ion, and, on the other hand, anions may be any of an inorganic anion or an organic anion concretely. for example, a halogen anion (for example, fluoride ion and chloride ion --), Bromide ion, iodide ion, permutation aryl sulfonic-acid ion For example, (p-toluenesulfonic-acid ion, p-chlorobenzene sulfonic-acid ion), aryl disulfon acid ion (for example, 1 and 3-benzene disulfon acid ion --) 1, 5-naphthalene disulfon acid ion, 2, 6-naphthalene disulfon acid ion, Alkyl-sulfuric-acid ion (for example, methylsulfuric acid ion), sulfate ion, thiocyanic acid ion, perchloric acid ion, tetrafluoroboric acid ion, picric-acid ion, acetic-acid ion, and trifluoro methansulfonic acid ion are mentioned.

[0075] Furthermore, an ionicity polymer or coloring matter, and other coloring matter that has a reverse charge may be used as a charge equilibrium counter ion, and metal complex ion (for example, bis-benzene -1, 2-JICHIORATO nickel (III)) is also possible.

[0076]

[Formula 10]
式 (V)



[0077] In a formula (V), D shows the aromatic series radical of at least four or more organic functions, and X1 and X2 express a sulfur atom, a selenium atom, CR 63R64, or CR65=CR66 independently, respectively. R63-R66 are a hydrogen atom or an alkyl group here, respectively. R61 and R62 are an alkyl group or an aromatic series radical, respectively, and P1 and P2 express a nonmetal atom group required to form poly methine coloring matter independently, respectively. A counter ion when a counter ion is required is shown in W2 neutralizing a charge.

[0078] It explains in more detail about a formula (V). D shows the aromatic series radical of at least four or more organic functions among a formula (V). As an example of such an aromatic series radical, benzene, naphthalene, an anthracene, a phenanthrene, etc. are mentioned as aromatic hydrocarbon with which these radicals are guided, anthraquinone, a carbazole, a pyridine, a quinoline, a thiophene, a furan, a xanthene, CHIANTOREN, etc. are mentioned as a terrorism ring to aromatic series, and these may have the substituent in addition to the joining segment. It is the induction radical of aromatic hydrocarbon preferably as an aromatic series radical expressed with D, and they are benzene or the induction radical of naphthalene still more preferably.

[0079] X1 and X2 are a sulfur atom or CR 63R64 preferably, and they are CR 63R64 most preferably.

[0080] P1 and P2 express a nonmetal atom group required to form poly methine coloring matter independently, respectively. Although it is also possible to form what kind of methine coloring matter, cyanine dye, merocyanine coloring matter, RODASHIANIN coloring matter, 3 nucleus merocyanine coloring matter, AROPORA coloring matter, a hemicyanine dye, styryl coloring matter, etc. are preferably mentioned by P1 and P2. Under the present circumstances, the substituent on the methine chain which forms coloring matter also contains in cyanine dye the thing in which the SUKUARIUMU ring and the crocodile NIUMU ring were formed. About the detail of these coloring matter F.M Harmer (F. M. Harmer) work "hetero cyclic party UNZU-cyanine soybean - and - RIREITIDO party UNZU () [Heterocyclic Compounds-Cyanine Dyes] and Related Compounds" and John Willie - and a - Suns (John Wiley & Sons)-new yoke, London, 1964 annual publications, Day em SUTAMA (D.) [M. Sturme] r) -- work -- " -- a hetero

cyclic party -- UNZU special TOPICS Inn hetero cyclic chemistry (Heterocyclic Compounds-Special topics in heterocyclic chemistry)" -- It is indicated by Chapter 18, Section 14, the 482nd to 515 tributes, etc. As for the formula of cyanine dye, merocyanine coloring matter, and RODASHIANIN coloring matter, what is shown in (XI) of the United States patent No. 5,340,694 the 21st and 22 tribute, (XII), and (XIII) is desirable. Moreover, the thing of the poly methine coloring matter formed of P1 and P2 which has a squarylium ring into one of methine chain parts at least is desirable, and what it has in both is still more desirable.

[0081] R61 and R62 are an aromatic series radical or an aliphatic series radical, and these may have the substituent. The carbon atomic numbers of an aromatic series radical are 5 thru/or 6 preferably [it is desirable and] to 5 thru/or 16, and a pan. The carbon atomic numbers of an aliphatic series radical are 1 thru/or 6 preferably [it is desirable and] to 1 thru/or 10, and a pan. As a non-permuted aliphatic series radical and an aromatic series radical, a methyl group, an ethyl group, n-propyl group, n-butyl, a phenyl group, a naphthyl group, etc. are mentioned.

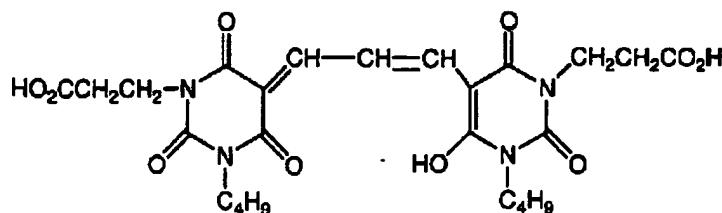
[0082] As for a formula (V), it is desirable to have an acidic group in at least one of R61, R62, P1, and P2. It is the substituent which has a dissociative proton, and as an example, a carboxylic acid, phosphonic acid, a sulfonic acid, a boric acid, etc. are mentioned, and an acidic group is a carboxylic acid preferably here. Moreover, such an acidic group may take the form which emitted and dissociated the proton.

[0083] W2 is synonymous with W1 of a formula (IV).
 [0084] Although the desirable example of poly methine coloring matter expressed with formula (II)- (V) below is shown, this invention is not limited to these. The coloring matter B, D, F, G, I, and K of example use is also mentioned.

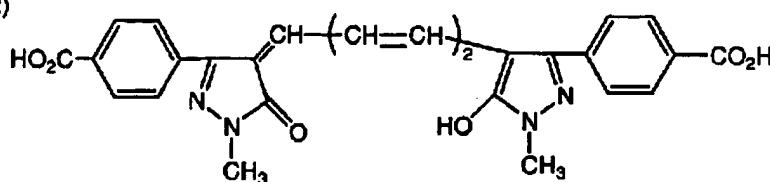
[0085]

[Formula 11]

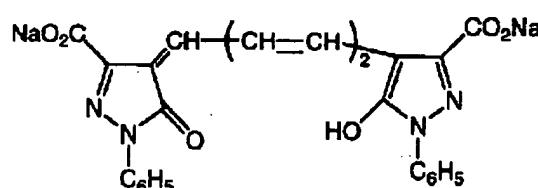
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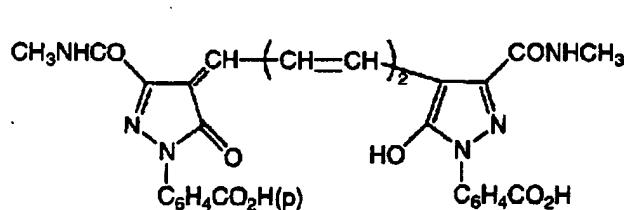
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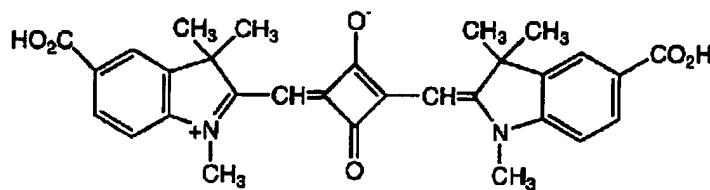
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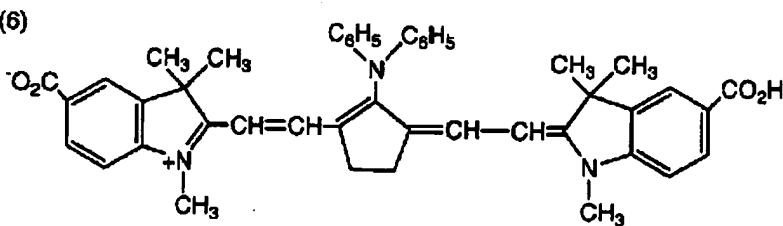
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(5)

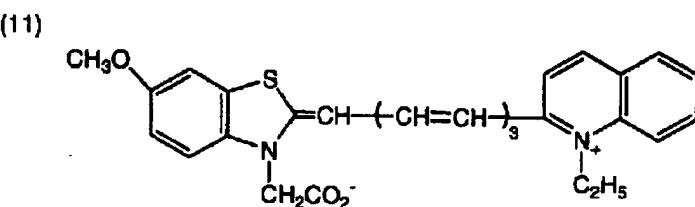
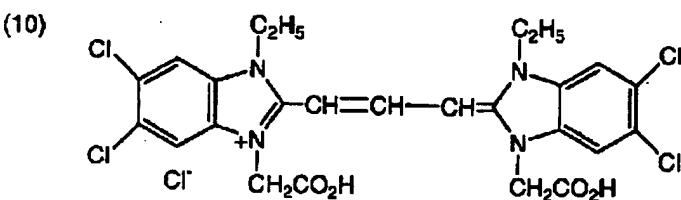
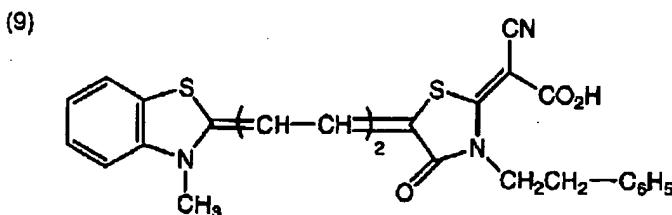
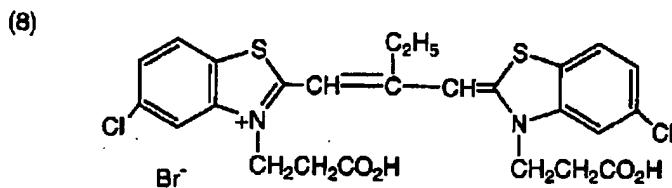
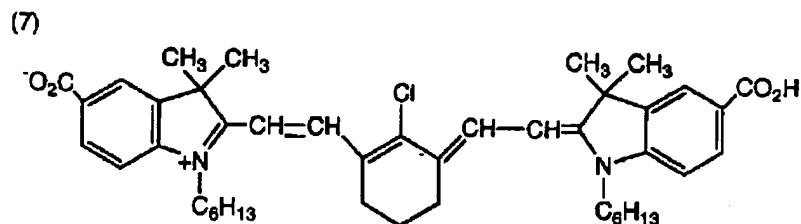


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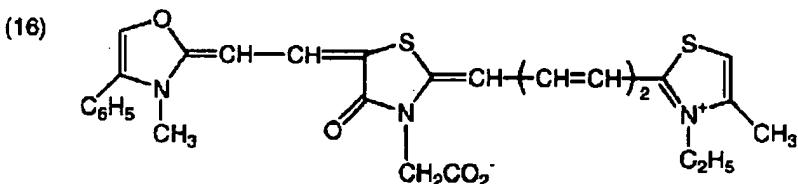
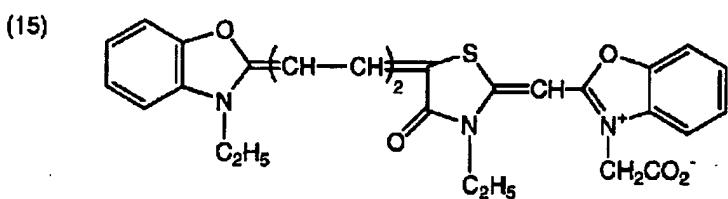
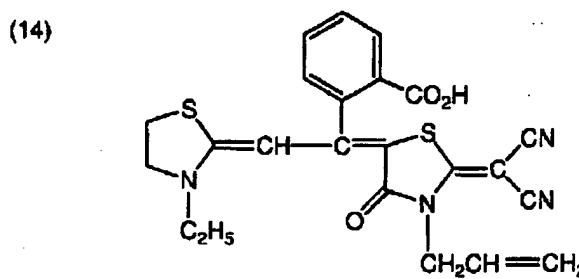
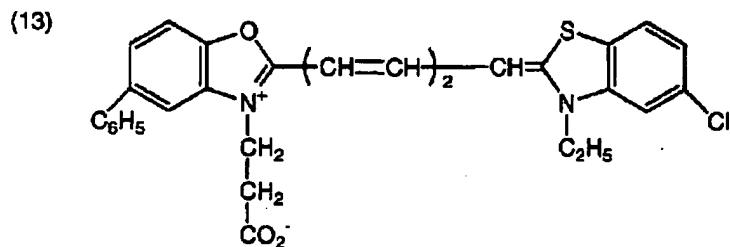
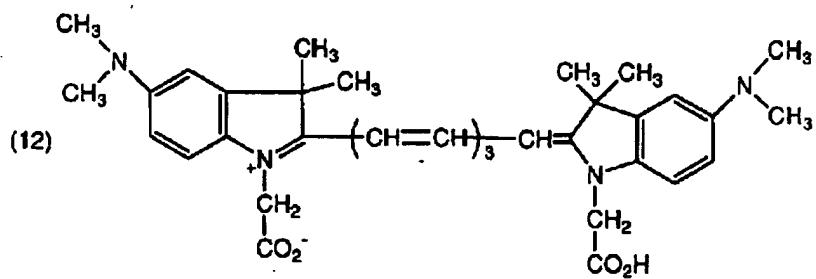


[0086]

[Formula 12]

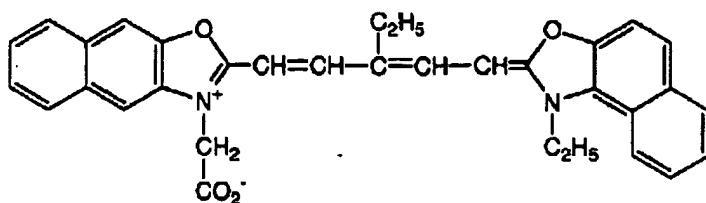


[0087]
[Formula 13]

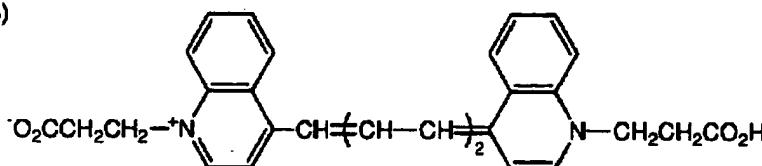


[0088]
[Formula 14]

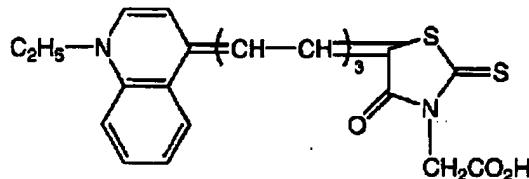
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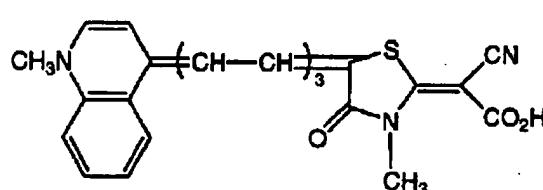
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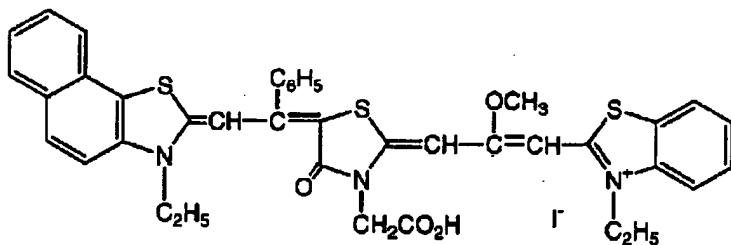
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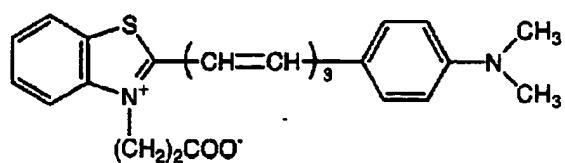
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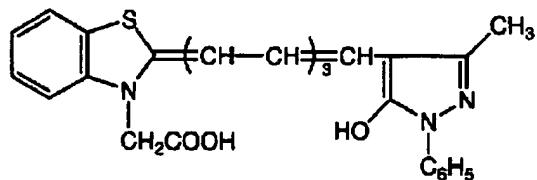
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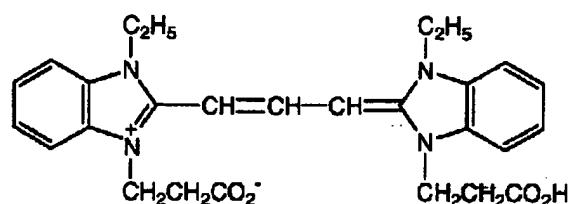
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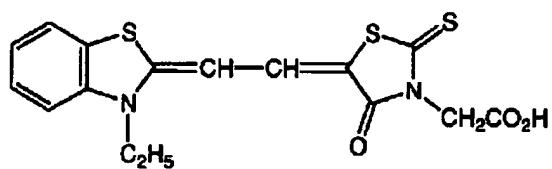
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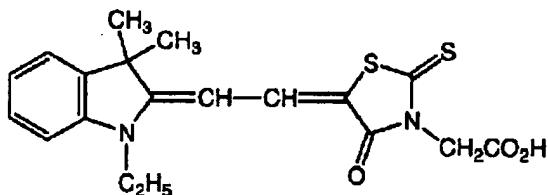
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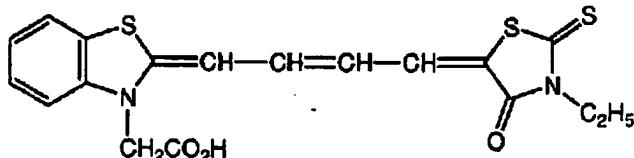
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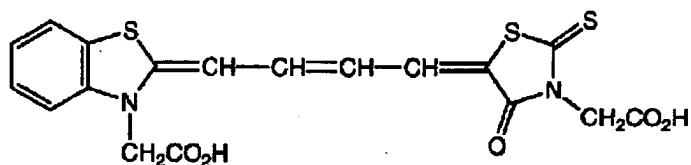
[0090]

[Formula 16]

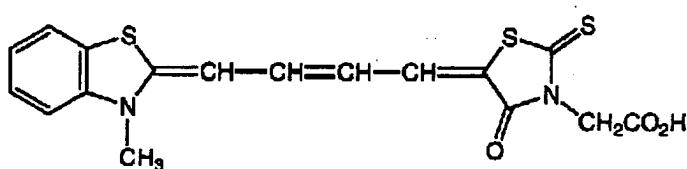
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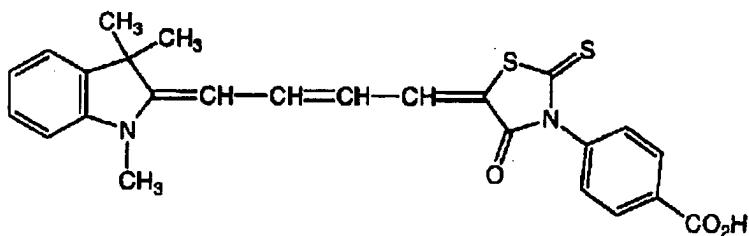
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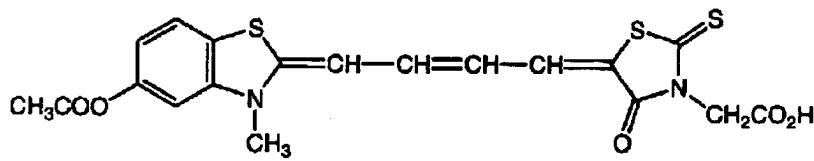
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(30)



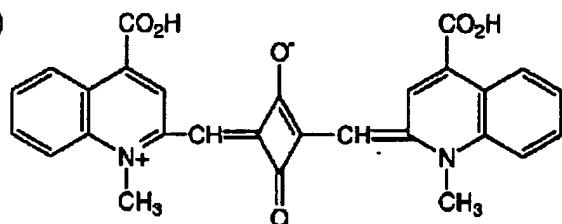
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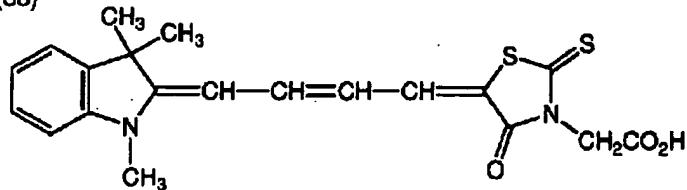
[0091]

[Formula 17]

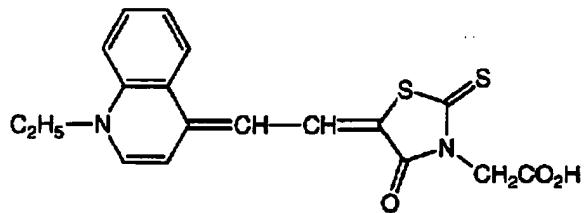
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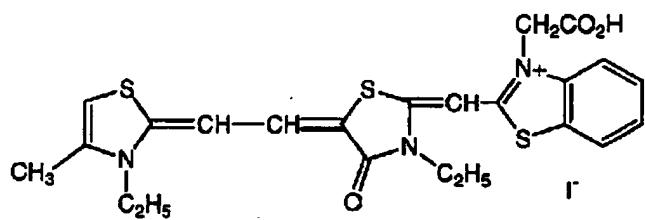
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(34)



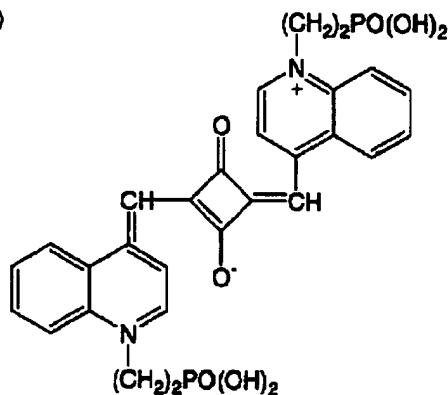
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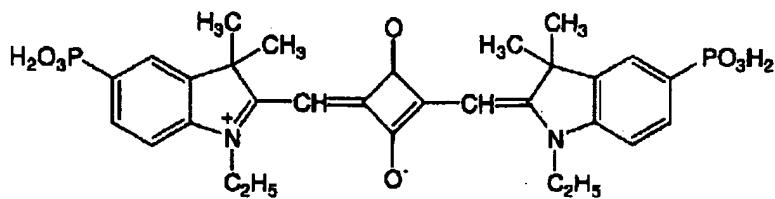
[0092]

[Formula 18]

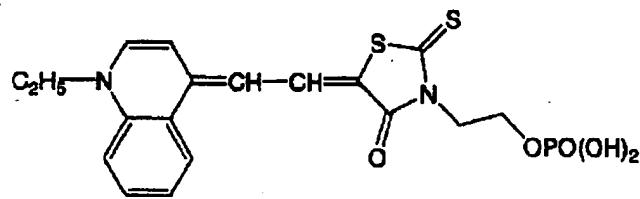
(36)



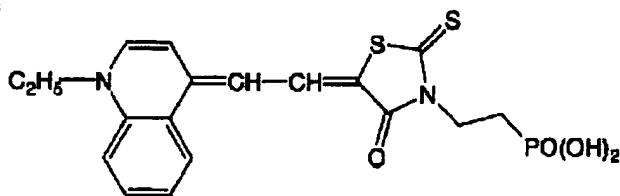
(37)



(38)



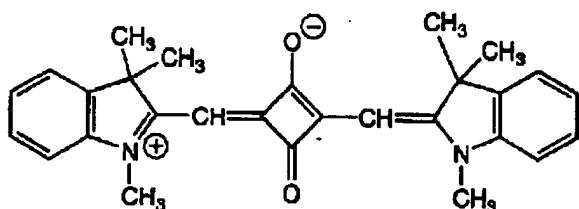
(39)



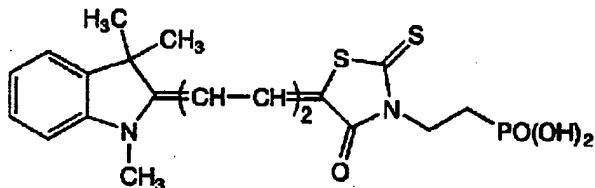
[0093]

[Formula 19]

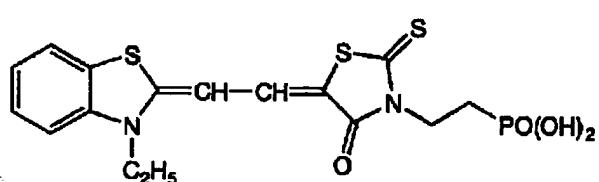
(40)



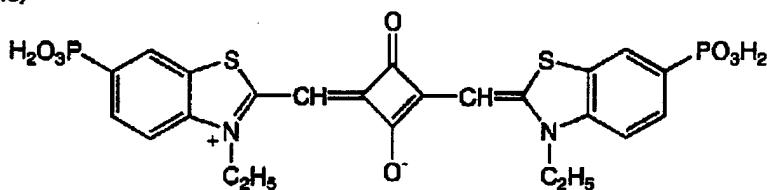
(41)



(42)

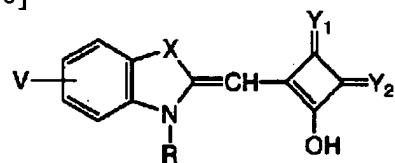


(43)



[0094]

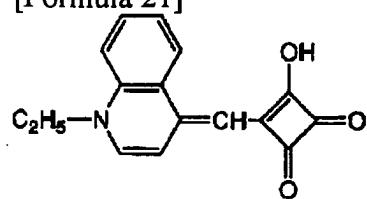
[Formula 20]



| 色素 | X | V | R | Y ₁ | Y ₂ |
|------|----------------------------------|----------|--------------------------------------|--------------------|--------------------|
| S-1 | C(CH ₃) ₂ | 4, 5-ベンゾ | C ₃ H ₇ | O | O |
| S-2 | C(CH ₃) ₂ | H | (CH ₂) ₃ COOH | O | O |
| S-3 | C(CH ₃) ₂ | 4, 5-ベンゾ | C ₂ H ₅ | S | S |
| S-4 | C(CH ₃) ₂ | 4, 5-ベンゾ | C ₂ H ₅ | C(CN) ₂ | O |
| S-5 | C(CH ₃) ₂ | 4, 5-ベンゾ | C ₂ H ₅ | C(CN) ₂ | C(CN) ₂ |
| S-6 | S | H | C ₂ H ₅ | O | O |
| S-7 | S | 5, 6-ベンゾ | CH ₃ | O | O |
| S-8 | O | H | CH ₃ | O | O |
| S-9 | Se | H | CH ₃ | O | O |
| S-10 | NC ₂ H ₅ | H | CH ₃ | O | O |
| S-11 | -CH=CH- | H | C ₂ H ₅ | O | O |

[0095]

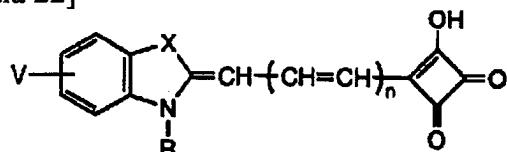
[Formula 21]



(S-12)

[0096]

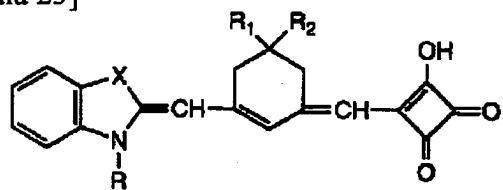
[Formula 22]



| 色素 | X | V | R | n |
|------|----------------------------------|-----------|-------------------------------|---|
| S-13 | C(CH ₃) ₂ | H | CH ₃ | 1 |
| S-14 | C(CH ₃) ₂ | 4, 5-ベンゾフ | C ₂ H ₅ | 1 |
| S-15 | S | H | CH ₃ | 2 |
| S-16 | S | 5, 6-ベンゾフ | C ₂ H ₅ | 3 |
| S-17 | S | 5, 6-ベンゾフ | C ₂ H ₅ | 4 |
| S-18 | O | H | CH ₃ | 1 |

[0097]

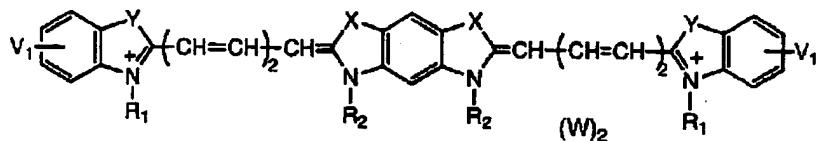
[Formula 23]



| 色素 | X | R ₁ | R ₂ | R |
|------|----------------------------------|-----------------|-----------------|--------------------------------------|
| S-19 | C(CH ₃) ₂ | CH ₃ | CH ₃ | C ₂ H ₅ |
| S-20 | S | CH ₃ | CH ₃ | C ₂ H ₅ |
| S-21 | O | CH ₃ | CH ₃ | (CH ₂) ₃ COOH |
| S-22 | O | Ph | H | C ₂ H ₅ |

[0098]

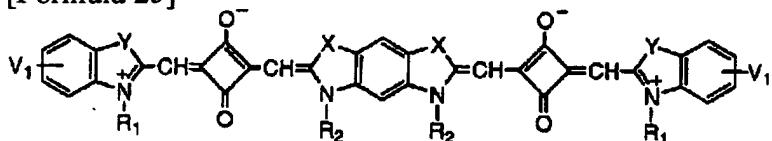
[Formula 24]



| 色素 | X | Y | R ₁ | R ₂ | V ₁ | W |
|------|----------------------------------|----------------------------------|--------------------------------------|-------------------------------|----------------|-----------------|
| S-23 | S | S | CH ₃ | CH ₃ | H | I ⁻ |
| S-24 | S | S | C ₂ H ₅ | CH ₃ | 5-COOH | I ⁻ |
| S-25 | C(CH ₃) ₂ | C(CH ₃) ₂ | CH ₃ | CH ₃ | 5-COOH | I ⁻ |
| S-26 | C(CH ₃) ₂ | C(CH ₃) ₂ | CH ₂ CH ₂ COOH | C ₂ H ₅ | H | Cl ⁻ |
| S-27 | O | C(CH ₃) ₂ | CH ₃ | C ₂ H ₅ | H | I ⁻ |

[0099]

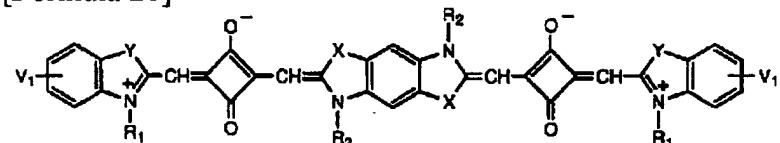
[Formula 25]



| 色素 | X | Y | R ₁ | R ₂ | V ₁ |
|------|----------------------------------|----------------------------------|-------------------------------|-------------------------------|-------------------|
| S-28 | S | C(CH ₃) ₂ | CH ₃ | CH ₃ | H |
| S-29 | S | C(CH ₃) ₂ | C ₃ H ₇ | CH ₃ | 4, 5-ベンゾ |
| S-30 | C(CH ₃) ₂ | S | CH ₃ | CH ₃ | 5-COOH |
| S-31 | C(CH ₃) ₂ | C(CH ₃) ₂ | CH ₃ | CH ₃ | 5-COOH |
| S-32 | C(CH ₃) ₂ | NCH ₃ | CH ₃ | C ₂ H ₅ | 5-CH ₃ |

[0100]

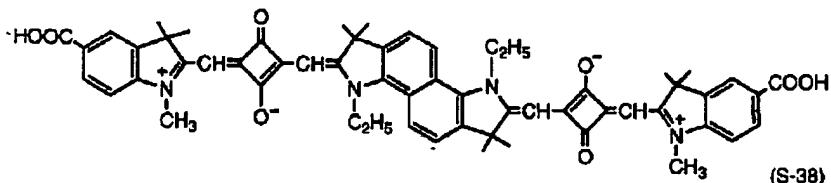
[Formula 26]



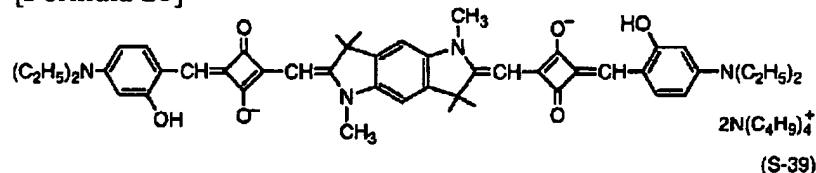
| 色素 | X | Y | R ₁ | R ₂ | V ₁ |
|------|----------------------------------|----------------------------------|--------------------------------------|-------------------------------|---------------------|
| S-33 | S | C(CH ₃) ₂ | CH ₃ | CH ₃ | H |
| S-34 | S | C(CH ₃) ₂ | C ₂ H ₅ | CH ₃ | 5-SO ₃ H |
| S-35 | C(CH ₃) ₂ | C(CH ₃) ₂ | CH ₃ | C ₂ H ₅ | 5-COOH |
| S-36 | C(CH ₃) ₂ | C(CH ₃) ₂ | CH ₂ CH ₂ COOH | CH ₃ | 4, 5-ベンゾ |
| S-37 | C(CH ₃) ₂ | NCH ₃ | CH ₃ | C ₂ H ₅ | 5-CH ₃ |

[0101]

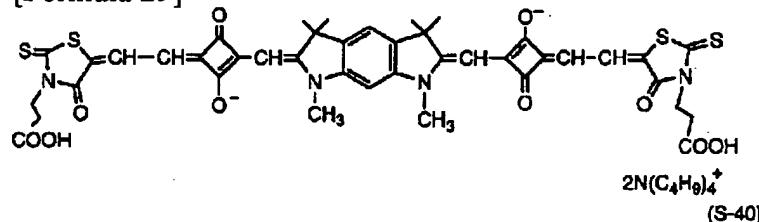
[Formula 27]



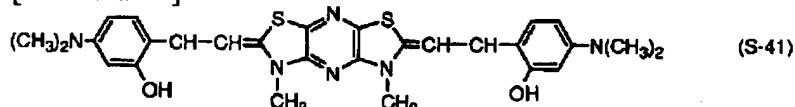
[0102]
[Formula 28]



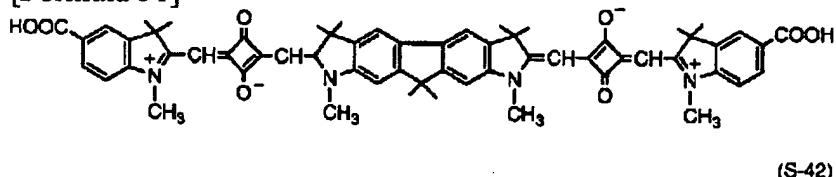
[0103]
[Formula 29]



[0104]
[Formula 30]



[0105]
[Formula 31]



[0106] The compound expressed with a formula (II) and a formula (III) F.M Harmer (F. M. Harmer) work "hetero cyclic party UNZU-cyanine soybean - and - RIREITIDO party UNZU () [Heterocyclic Compounds-Cyanine Dyes] and RelatedCompounds" and John Willie - and - Suns (John Wiley & Sons)-New York, London, 1964 annual publications, "hetero written by day em SUTAMA (D. M. Sturmer) -- cyclic and party UNZU special TOPICS Inn hetero cyclic chemistry () [Heterocyclic Compounds-Special] topics in heterocyclic chemistry", Chapter 18, Section 14, the 482nd to 515 term, John Willie -, and - Suns (John Wiley & Sons)-New York, London, 1977 annual publications, "ROZZU chemistry OBU carbon party UNZU (Rodd's Chemistry of Carbon Compounds)" 2nd.Ed.vol.IV, partB, 1977 **, Chapter 15, the 369th to 422 term, Based on the approach of a publication, it is compoundable to ERUSEBIA Science public company ink (Elsevier Science Publishing Company Inc.) company **, New York, the British patent No. 1,077,611, etc.

[0107] composition of the compound expressed with the formula (IV) used for this invention -- Dyes and Pigments -- it refers to the publication of the 21st volume reference, such as 227-234 etc. pages, and it can be performed. Moreover, composition of the compound expressed with a formula (V) is Ukrainskii Khimicheskii Zhurnal. 40th volume No. 3 253-258 pages and Dyes and Pigments It refers to the publication of the reference quoted in 21st volume 227-234 pages and these reference etc., and it can be performed.

[0108] The method of making coloring matter stick to a semi-conductor particle can use the approach of being immersed, or applying a coloring matter solution to a semi-conductor particle layer, and making the working electrode which painted the often dried semi-conductor particle into the coloring matter solution adsorbing it. In the case of the

former, dip coating, a dip method, a roller, the Ayr knife method, etc. can be used. As the latter method of application, there are the wire bar method, the slide hopper method, the extrusion method, the curtain method, the spin method, and a spray method, and there are letterpress, offset, gravure, screen-stencil, etc. as the printing approach. After painting a spacer layer on a semi-conductor particle layer in this invention, it is desirable to make coloring matter stick to a semi-conductor particle by the former approach.

[0109] Like the time of formation of a semi-conductor particle layer, in a viscous liquid (for example, 0.01 - 500 Poise), various print processes besides the extrusion method are suitable, the slide hopper method, the wire bar method, or the spin method is suitable with hypoviscosity liquid (for example, 0.1 or less Poises), and liquid viscosity can also be made the uniform film.

[0110] Thus, what is necessary is just to choose a grant method suitably corresponding to parameters, such as liquid viscosity of coloring matter coating liquid, coverage, a base material, and a spreading rate. When fertilization is considered, as short the one of the time amount which the coloring matter adsorption after spreading takes as possible is good.

[0111] Since existence of non-adsorbed coloring matter becomes the disturbance of the component engine performance, removing by washing promptly after adsorption is desirable. It is good to use a wet washing tub and for an organic solvent like polar solvents, such as an acetonitrile, and an alcohols solvent to wash. Moreover, in order to increase the amount of adsorption coloring matter, it is desirable to carry out, before adsorbing heat-treatment. After heat-treatment, in order to avoid that water sticks to a semi-conductor particle front face, it is desirable not to return to ordinary temperature but to also make coloring matter adsorb quickly among 40-80 degrees C.

[0112] The amount of the coloring matter used is the whole, and its 0.01-100m mol is [1m of base materials] desirable per two. Moreover, the amount of adsorption to the semi-conductor particle of coloring matter has desirable 0.01-1m mol to 1g of semi-conductor particles. By considering as such an amount of coloring matter, the sensitization effectiveness in a semi-conductor is fully acquired. On the other hand, if there are few amounts of coloring matter, the sensitization effectiveness will become inadequate, and if there are too many amounts of coloring matter, it will become the cause by which the coloring matter which has not adhered to a semi-conductor floats, and the sensitization effectiveness is reduced.

[0113] Moreover, coadsorption of the compound colorless for the purpose which reduces the interaction of coloring matter, such as a meeting, may be carried out. The steroid compound (for example, cholic acid) which has a carboxy group as a hydrophobic compound which carries out coadsorption is mentioned. Moreover, an ultraviolet ray absorbent can also be used together.

[0114] Moreover, after adsorbing coloring matter, amines may be used and the front face of a semi-conductor particle may be processed, in order to promote removal of excessive coloring matter. As desirable amines, a pyridine, a 4-tert-butyl pyridine, polyvinyl pyridine, etc. are mentioned. When these are liquids, you may use as it is, and may dissolve and use for an organic solvent.

[0115] Hereafter, a charge transfer layer and a counter electrode are explained in detail. A charge transfer layer is a layer which has the function to supplement the oxidant of coloring matter with an electron. The so-called gel electrolyte which sank into the polymer matrix the liquid (electrolytic solution) which dissolved the redox couple in the organic solvent as an example of the typical charge transfer layer which can be used by this invention, and the liquid which dissolved the redox couple in the organic solvent, the fused salt containing a redox couple, etc. are mentioned. Furthermore, a solid electrolyte and an electron hole (hole) transportation ingredient can also be used.

[0116] As for the electrolytic solution used by this invention, it is desirable to consist of an electrolyte, a solvent, and an additive. The electrolyte of this invention is the combination (it LiI(s) as an iodide) of I₂ and an iodide. A metal iodide or tetra-alkylammonium iodide, such as NaI, KI, CsI, and CaI₂, The iodine salt of the 4th class ammonium compounds, such as pyridinium iodide and imidazolium iodide, etc., Combination of Br₂ and a bromide (it LiBr(s) and NaBr(s) as a bromide) KBr, CsBr, and CaBr₂ etc. -- a metal bromide or a tetra-alkylammonium star's picture -- The others which are the bromine salt of the 4th class ammonium compounds, such as a pyridinium star's picture, etc., Sulfur compounds, such as metal complexes, such as a ferrocyanic acid salt-ferricyanic acid salt and ferrocene-ferricinium ion, sodium polysulfide, and alkyl thiol-alkyl disulfide, viologen coloring matter, a hydroquinone-quinone, etc. can be used. The electrolyte which combined the iodine salt of the 4th class ammonium compounds, such as I₂, LiI, and pyridinium iodide, imidazolium iodide, also in this is desirable in this invention. The electrolyte mentioned above may be mixed and used. moreover, an electrolyte -- EP-718288 No., WO 95/No. 18456, J.Electrochem.Soc., Vol.143, and No. -- the salt (fused salt) of a melting condition can also be used at 10, 3099 (1996), Inorg.Chem.1996, 35, and the room temperature indicated by 1168-1178. A solvent may not be used when using fused salt as an electrolyte.

[0117] Desirable electrolytic concentration is less than [more than 0.1M15M], and is less than [10M] more than 0.2

M still more preferably. Moreover, the addition concentration of the desirable iodine in the case of adding iodine to an electrolyte is less than [more than 0.01M0.5M].

[0118] As for the solvent used for an electrolyte by this invention, it is desirable for a dielectric constant to be high in improving ionic mobility low, and for viscosity to be the compound which improves effective carrier concentration and can discover the outstanding ion conductivity. As such a solvent, carbonate compounds, such as ethylene carbonate and propylene carbonate, Heterocyclic compounds, such as 3-methyl-2-oxazolidinone, dioxane, Ether compounds, such as diethylether, ethylene glycol dialkyl ether, The propylene glycol dialkyl ether, the polyethylene-glycol dialkyl ether, Chain-like ether, such as the polypropylene-glycol dialkyl ether, A methanol, ethanol, ethylene glycol monoalkyl ether, Propylene glycol monoalkyl ether, polyethylene-glycol monoalkyl ether, Alcohols, such as polypropylene-glycol monoalkyl ether, Ethylene glycol, propylene glycol, a polyethylene glycol, Polyhydric alcohol, such as a polypropylene glycol and a glycerol, an acetonitrile, Non-proton polar substances, such as nitrile compounds, such as guru taro dinitrile, a methoxy acetonitrile, propionitrile, and a benzonitrile, dimethyl sulfoxide (DMSO), and sulfolane, water, etc. can be used.

[0119] Moreover, at this invention, it is J.Am.Ceram.Soc. and 80. (12) Basic compounds, such as a ter-butyl pyridine which is indicated by 3157-3171 (1997), and 2-picoline, 2, and 6-lutidine, can also be added. The desirable density range in the case of adding a basic compound is less than [more than 0.05M2M].

[0120] It can also be used in this invention, making an electrolyte able to gel by technique containing polymer addition, oil gelling agent addition, and polyfunctional monomer, such as a polymerization and crosslinking reaction of a polymer, (solid state). Although the compound indicated by **Polymer Electrolyte Revi ews -1 and 2** (J. coeditorship of R.MacCallum and C.A.Vincent, ELSEVIER APPLIED SCIENCE) can be used when making it gel by polymer addition, especially a polyacrylonitrile and polyvinylidene fluoride can be used preferably. When making it gel by oil gelling agent addition, J.Chem Soc.Japan, Ind.Chem.Soc., 46779 (1943), J.Am.Chem.Soc., 111, 5542 (1989), J.Chem.Soc., Chem.Com mun., 1993, 390, Angew.Chem.Int.Ed.Engl., 35, 1949 (1996), Although Chem.Lett., 1996, 885, J.Chm.Soc., Chem.Commun., 1997, and the compound indicated by 545 can be used, a desirable compound is a compound which has amide structure in the molecular structure.

[0121] When forming a gel electrolyte by the polymerization of polyfunctional monomer, the approach of making it gel by preparing a solution from polyfunctional monomer, a polymerization initiator, an electrolyte, and a solvent, forming a sol-like electrolyte layer on the electrode which supported coloring matter by approaches, such as the cast method, the applying method, dip coating, and the sinking-in method, and carrying out a radical polymerization after that is desirable. A divinylbenzene, ethylene glycol dimethacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene-glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, a pentaerythritol thoria chestnut rate, and trimethylolpropane triacrylate are mentioned preferably [that it is the compound which has two or more ethylene nature partial saturation radicals] by the polyfunctional monomer as a desirable example. In addition to this, the monomers which constitute a gel electrolyte may contain the monofunctional monomer. the ester guided from an acrylic acid or alpha-alkyl acrylic acids (for example, methacrylic acid etc.), or amides (for example, N-iso-propyl acrylamide --) Acrylamide, 2-acrylamido-2-methyl propane sulfonic acid, Acrylamidepropyl trimethylammoniumchloride, methyl acrylate, Hydroxyethyl acrylate, n-propylacrylate, n-butyl acrylate, 2-methoxy ethyl acrylate, cyclohexyl acrylate, etc., the ester (for example, maleic-acid dimethyl --) guided from vinyl ester (for example, vinyl acetate), a maleic acid, or a fumaric acid Maleic acids, such as dibutyl maleate and diethyl fumarate, a fumaric acid, The sodium salt of p-styrene sulfonic acid, acrylonitrile, a methacrylonitrile, Dienes (for example, a butadiene, a cyclopentadiene, an isoprene) An aromatic series vinyl compound (for example, styrene, p-KURORU styrene, styrene sulfonic-acid sodium), The vinyl compound which has nitrogen-containing heterocycle, the vinyl compound which has quarternary ammonium salt, N-vinyl formamide, an N-vinyl-N-methyl formamide, a vinyl sulfonic acid, Sodium vinylsulfonate, vinylidene fluoride, vinylidene chloride, vinyl alkyl ether (for example, methyl vinyl ether), ethylene, a propylene, 1-butene, isobutene, N-phenyl maleimide, etc. can be used preferably. It is desirable still more desirable that it is [0.5 % of the weight or more] 70 or less % of the weight, and the desirable weight composition range of a polyfunctional monomer occupied in the monomer whole quantity is 50 or less % of the weight 1.0 % of the weight or more.

[0122] The polymerization of the above-mentioned monomer can be carried out according to the radical polymerization which is the general giant-molecule synthesis method indicated by the laboratory procedure (Kagaku-Dojin) of Takayuki Otsu and Kinoshita **** collaboration:giant-molecule composition, Takayuki Otsu:lecture polymerization reaction theory 1 radical polymerization (I), and (Kagaku-Dojin). It is desirable heating, light, an electron ray, and to carry out the radical polymerization especially of the monomer for gel electrolytes which can be used by this invention with heating, although a radical polymerization can be carried out electrochemically. The polymerization initiators preferably used when a crosslinked polymer is formed by heating are peroxide system initiators, such as azo system

initiators, such as 2,2'-azobis isobutyronitrile, 2, and 2'-azobis (2,4-dimethylvaleronitrile), dimethyl 2, and 2'-azobis (2-methyl propionate) (dimethyl 2, 2'-azobisisobutyrate), and benzoyl peroxide, etc. The desirable addition of a polymerization initiator is 20 or less % of the weight 0.01 % of the weight or more to a monomer total amount, and is 10 or less % of the weight 0.1 % of the weight or more still more preferably.

[0123] It is desirable still more desirable that it is [0.5 % of the weight or more] 70 or less % of the weight, and the weight composition range of monomers occupied to a gel electrolyte is 50 or less % of the weight 1.0 % of the weight or more.

[0124] Moreover, when making an electrolyte gel by the crosslinking reaction of a polymer, it is desirable to use together the polymer and cross linking agent containing the reactant radical which can construct a bridge. In this case, the reactant radicals in which desirable bridge formation is possible are nitrogen-containing heterocycles (for example, a pyridine ring, an imidazole ring, a thiazole ring, an oxazole ring, a triazole ring, a morpholine ring, a piperidine ring, a piperazine ring, etc.), and desirable cross linking agents are reagents (for example, alkyl halide, a halogenation aralkyl, a sulfonate, an acid anhydride, acid chloride, isocyanate, etc.) of two or more organic functions in which an electrophilic reaction is possible to a nitrogen atom.

[0125] In this invention, the electron hole transportation ingredient which combined organic, inorganic, or these both instead of the electrolyte can be used. As an organic electron hole transportation ingredient applicable to this invention N, N'-diphenyl-N, N'-screw (4-methoxyphenyl) - (1 and 1'-biphenyl) -4, 4'-diamine (J. Hagen et al., Synthetic Metal 89 (1997) 215-220), 2, 2', 7, a 7'- tetrakis (N and N-G p-methoxy phenylamine) 9 and 9'-Spirobi fluorene (Nature, Vol.395, 8 Oct.1998, p583-585, and WO 97/10617), The aromatic series diamine compound which connected the 3rd class aromatic amine unit of 1 and 1-screw {4-(G p-tolylamino) phenyl} cyclohexane (JP,59-194393,A), 4, 4, the aromatic amine that two or more fused aromatic rings permuted by the nitrogen atom including two or more tertiary amine represented with - screw [(N-1-naphthyl) -N-phenylamino] biphenyl (JP,5-234681,A), the aromatic series triamine (U.S. Pat. No. 4,923,774 --) which has starburst structure with the derivative of triphenyl benzene JP,4-308688,A, N, N'-diphenyl-N, N'-screw (3-methylphenyl) - (1 and 1'-biphenyl) Aromatic series diamines, such as -4 and 4'-diamine (U.S. Pat. No. 4,764,625), alpha, alpha, alpha', alpha'-tetramethyl - alpha, alpha'-screw (4-G p-tolylamino phenyl)-para xylene (JP,3-269084,A), As a p-phenylene diamine derivative and the whole molecule, a triphenylamine derivative unsymmetrical in three dimensions (JP,4-129271,A), The compound which the aromatic series diamino radical permuted by the pyrenyl radical (JP,4-175395,A), The aromatic series diamine which connected the 3rd class aromatic amine unit by ethylene (JP,4-264189,A), The aromatic series diamine which has styryl structure (JP,4-290851,A), A benzyl phenyl compound (JP,4-364153,A), the thing which connected tertiary amine by the fluorene radical (JP,5-25473,A), A triamine compound (JP,5-239455,A), a pith dipyridyl amino biphenyl (JP,5-320634,A), N, N, and N-triphenylamine derivative (JP,6-1972,A), The aromatic series diamine which has FENO affected gin structure (Japanese Patent Application No. No. 290728 [five to]), The aromatic amines shown in a diamino phenyl phenanthridine derivative (Japanese Patent Application No. No. 45669 [six to]) etc. An alpha-octyl thiophene and alpha, and omega-dihexyl-alpha-octyl thiophene (Adv.Mater.1997, 9, N 0.7, p557), A hexa dodecyl DODESHI thiophene (Angew.Chem.Int.Ed.Engl.1995, 34, No.3, p303-307), Oligo thiophene compounds, such as 2, 3-b:6, and 2 and 8-dihexyl ANSURA [7-b'] dithio FEN (4 N0. 1998p JACS, Vol120, 664 -672), Polypyrrole (K.Murakoshi et al.,;Chem.Lett.1997, p471), ** Handbook of Organic Conductive Molecules and Polymers Vol.1, 2 and 3, and 4** (NALWA work --) The polyacetylene indicated by WILEY publication and its derivative, Pori (p-phenylene) And the derivative and Pori (p-phenylenevinylene) And the derivative, Conductive polymers, such as poly thiylene vinylene and its derivative, the poly thiophene and its derivative, the poly aniline and its derivative, the poly toluidine, and its derivative, can be used preferably. moreover In order to control dopant level into an organic electron hole (hole) transportation ingredient as indicated by Nature, Vol.395, 8 Oct.1998, and p583-585 Add the compound containing a cation radical like tris (4-BUROMO phenyl) aminium hexa chloro antimonate, or In order to perform potential control on the front face of an oxide semiconductor (compensation of a space charge layer), a salt like Li [(CF₃SO₂)₂Ns] may be added.

[0126] An organic electron hole transportation ingredient can be introduced into the interior of an electrode by technique, such as a vacuum deposition method, the cast method, the applying method, a spin coat method, dip coating, an electrolytic polymerization method, and a photoelectrical depolymerization method. Moreover, when using an electron hole transportation ingredient instead of the electrolytic solution, it is desirable to paint a titanium-dioxide thin layer as an under coat using technique, such as spray pyrolysis indicated by Electorochim.Acta 40 and 643-652 (1995) for short circuit prevention.

[0127] When using an inorganic solid-state compound instead of an electrolyte, copper iodide (p-CuI) (J.Phys.D:Appl.Phys.31 (1998) 1492-1496), thiocyanogen-ized copper (Thin Solid Films 261 (1995) 307-310 and J.Appl.Phys. -- 80 (8) -- 15 October 1996, p4749-4754, Chem.Mater.1998, 10, 1501-1509, Semicond.Sci.Technol.10,

1689-1693, etc. The cast method, the applying method, a spin coat method, It can introduce into the interior of an electrode by technique, such as dip coating and electrolysis plating.

[0128] Two kinds of approaches can be considered about the formation approach of a charge transfer layer. One is the approach of sticking a counter electrode previously on a spacer layer, and putting a liquefied charge transfer layer between the gap. Another is the approach of giving a direct charge transfer layer on a spacer layer, and a counter electrode will be given after that.

[0129] The vacuum process which makes it a pressure lower than the ordinary pressure process and ordinary pressure which use the capillarity by immersion etc. as an approach to put the charge transfer layer in the case of the former, and permutes a gaseous phase by the liquid phase can be used.

[0130] In the case of the latter, in a wet charge transfer layer, a counter electrode will be given with un-drying, and the liquid leakage control measure of the edge section will also be taken. Moreover, there is also the approach of applying with wet in the case of a gel electrolyte, and solidifying by approaches, such as a polymerization, and a counter electrode can also be given after drying and fixing in that case. as the approach of giving a wet organic electron hole transportation ingredient besides the electrolytic solution, and a gel electrolyte -- grant of a semi-conductor particle content layer or coloring matter -- the same -- dip coating, a roller, a dip method, the Ayr knife method, the extrusion method, the slide hopper method, and WAYABA -- law, the spin method, a spray method, the cast method, various print processes, etc. can be considered. In the case of the electron hole (hole) transportation ingredient of a solid electrolyte or a solid-state, a charge transfer layer can be formed by dry membrane formation processing of a vacuum deposition method, a CVD method, etc., and a counter electrode can also be given after that.

[0131] When considering fertilization, although correspondence is also possible by closing an edge part promptly after painting in the case of the electrolytic solution which cannot be solidified, or a wet electron hole transportation ingredient, after carrying out film formation of the electron hole transportation layer by wet grant, it is more desirable in the case of the electron hole transportation ingredient which can be solidified to solidify by approaches, such as photopolymerization and a heat radical polymerization. Thus, what is necessary is just to choose a film grant method suitably according to liquid nature or process conditions.

[0132] In addition, as moisture in a charge transfer layer, 10,000 ppm or less are 2,000 ppm or less desirable still more preferably, and is 100 ppm or less especially preferably.

[0133] A counter electrode works as a positive electrode of a photoelectrochemical cell, when an optoelectric transducer is used as a photoelectrochemical cell. Although a counter electrode can also usually use the above-mentioned conductive base material and the base material which has a conductive layer similarly, a base material is not necessarily required of a configuration at which reinforcement and sealing performance are fully maintained. As a conductive ingredient concretely used for a counter electrode, a metal, carbon (for example, platinum, gold, silver, copper, aluminum, a rhodium, an indium, etc.), or conductive metallic oxides (what doped the fluorine to an indium-tin multiple oxide and the tin oxide) are mentioned. Although there is especially no limit, as for the thickness of a counter electrode, it is desirable that it is [3nm or more] 10 micrometers or less. When it is a metallic material, the thickness is 5 micrometers or less preferably, and 5nm or more range of it is 3 micrometers or less still more preferably.

[0134] In order for light to reach a sensitization layer, at least the above-mentioned conductive base material and one side of a counter electrode must be substantially transparent. In the photoelectrochemical cell of this invention, a conductive base material is transparent and it is desirable to carry out incidence of the sunlight from a base material side. In this case, as for a counter electrode, it is still more desirable to have the property to reflect light. The glass which vapor-deposited a metal or conductive oxide as a counter electrode in this invention, plastics, or a metal thin film can be used.

[0135] As grant of a charge transfer layer described painting of a counter electrode, it is 2 passage in the case of giving on a spacer layer previously with the case where it gives on a charge transfer layer. In any case, counter electrode material can be suitably formed by approaches, such as spreading, a lamination, vacuum evaporationo, and lamination, on a charge transfer layer or a semi-conductor particle content layer the class of counter electrode material, and the class of charge transfer layer. For example, when sticking a counter electrode, the substrate in which the above-mentioned conductive ingredient was prepared as a conductive layer by technique, such as spreading, vacuum evaporationo, and CVD, can be stuck. Moreover, when a charge transfer layer is a solid-state, a counter electrode can be directly formed for the above-mentioned conductive ingredient by technique, such as spreading, plating, and PVD, CVD, on it.

[0136] Furthermore, it is also possible to prepare the layer of the function of an and also [it is need, such as a protective layer and an antireflection film,] in the conductive base material or counter electrode of a working electrode. When carrying out functional separation of such a layer in a multilayer, applying by coincidence multilayer spreading or serial is possible, but when priority is given to productivity, coincidence multilayer spreading is more desirable. In

coincidence multilayer spreading, when productivity and film grant homogeneity are considered, the slide hopper method and the extrusion method are suitable. Moreover, these stratum functionale can also be prepared with the ingredient using technique, such as vacuum evaporationo and attachment.

[0137] In order to prevent degradation of a structure and the vaporization of contents in the photoelectrochemical cell of this invention, it is desirable to seal the side face of a cell with a polymer, adhesives, etc.

[0138] Next, the cellular structure and module structure in the case of applying the optoelectric transducer of this invention to the so-called solar battery are explained.

[0139] Although the structure inside the cel of a coloring matter sensitization mold solar battery is the same as the optoelectric transducer and photoelectrochemical cell which were mentioned above, as shown in drawing 2 or drawing 3 , it is doubled with the purpose and various gestalten are fundamentally possible for it. If it roughly divides into two, they will be the structure [drawing 2 (a), (d), and drawing 3 (g)] in which the incidence of both sides to light is possible, and a type [drawing 2 (b), (c), drawing 3 (e) and (f), and (h)] possible only from one side.

[0140] the coloring matter adsorption TiO two-layer two-layer drawing 2 (a) is a coloring matter adsorption semi-conductor particle content layer between the transparency conductive layers 12 -- it is the structure where 14, and the spacer layer 10 and the charge transfer layer 11 were made to intervene. drawing 2 (b) -- the transparency substrate 13 top -- a part -- the metal lead 9 -- preparing -- further -- the transparency conductive layer 12 -- preparing -- coloring matter adsorption TiO two-layer -- it is the structure which formed 14, the spacer layer 10, the charge transfer layer 11, and the metal layer 8 in this order, and has arranged the support substrate 15 further. drawing 2 (c) -- the support substrate 15 top -- further -- the metal layer 8 -- having -- coloring matter adsorption TiO two-layer -- it is the structure which carried out the metal lead 9 side inside, and has arranged the transparency substrate 13 which formed 14 and the spacer layer 10, formed the charge transfer layer 11 and the transparency conductive layer 12 further, and formed the metal lead 9 in the part. although drawing 2 (d) established the metal lead 9 in part on the transparency substrate 13 and the transparency conductive layer 12 was formed further -- between -- coloring matter adsorption TiO two-layer -- it is the structure where 14, the spacer layer 10, and the charge transfer layer 11 were made to intervene. drawing 3 (e) -- the transparency substrate 13 top -- the transparency conductive layer 12 -- having -- coloring matter adsorption TiO two-layer -- it is the structure which formed 14 and the spacer layer 10, formed the charge transfer layer 11 and the metal layer 8 further, and has arranged the support substrate 15 on this. drawing 3 (f) -- the support substrate 15 top -- the metal layer 8 -- having -- coloring matter adsorption TiO two-layer -- it is the structure which formed 14 and the spacer layer 10, formed the charge transfer layer 11 and the transparency conductive layer 12 further, and has arranged the transparency substrate 13 on this. between the transparency substrates 13 with which drawing 3 (g) has the transparency conductive layer 12 -- the transparent conductive layer 12 -- the inside -- carrying out -- coloring matter adsorption TiO two-layer -- it is the structure where 14, the spacer layer 10, and the charge transfer layer 11 were made to intervene. drawing 3 (h) -- the support substrate 15 top -- the metal layer 8 -- preparing -- coloring matter adsorption TiO two-layer -- it is the structure of forming 14 and the spacer layer 10, forming the solid charge transfer layer 16 further, and having the metal layer 8 or the metal lead 9 in part on this.

[0141] The module structure of the coloring matter sensitization mold solar battery of this invention can take the same structure as fundamentally as the conventional solar cell module. Although it can consider as the structure of a cel being constituted on support substrates, such as a metal and a ceramic, covering a it top with restoration resin, cover glass, etc. generally, and incorporating light from the opposite side of a support substrate, it is also possible to use transparent materials, such as tempered glass, for a support substrate, to constitute a cel on it, and to incorporate light from the support substrate side of the transparency. Module structures, such as substrate one apparatus specifically used with module structure or an amorphous-silicon solar cell called a super straight type, a substrate type, and a potting type, are possible. Such module structures can be suitably chosen by the purpose of use or the service space (environment). The example which carried out the modularization of the component of this invention by substrate one apparatus is shown in drawing 4 .

[0142] the structure of drawing 4 -- one field top of the transparency substrate 13 -- the transparency conductive layer 12 -- having -- a this top -- coloring matter adsorption TiO two-layer -- the modularization of the cel which formed the spacer layer 10, the solid charge transfer layer 16, and the metal layer 8 further is carried out to 14, and the acid-resisting layer 17 is formed in the field of another side of the transparency substrate 13. in this case, the coloring matter adsorption TiO two-layer which is the sensitization section in order to raise the use effectiveness of incident light -- it is more desirable to enlarge the rate of surface ratio of 14 (rate of surface ratio when seeing from the transparency substrate 13 side which is the plane of incidence of light).

[0143] The typical structure a super straight type and substrate type has one side or transparent both sides , and between the support substrates to which acid-resisting processing was performed , a cel is arrange , between adjacent cels is connect to fixed spacing by a metal lead or flexible wiring , and it is the structure which takes out outside the power

which has arranged the current collection electrode in the rim section, and was generated in it. Between a substrate and a cel, the plastic material of various classes, such as ethylene vinyl acetate (EVA), can be used in the form of a film or restoration resin according to the purpose for protection of a cel or a current collection effectiveness rise. Moreover, when a hard material uses front faces, such as a place with few impacts from the outside, from a location without the wrap need, it is also possible by constituting a surface protective layer from transparency plastic film, or stiffening the above-mentioned restoration and closure ingredient to give a protection feature and to lose the support substrate of one side. The perimeter of a support substrate is fixed in the shape of sandwiches with a metal frame for internal seal and modular rigid reservation, and the seal seal of between a support substrate and a frame is carried out with a sealing agent.

[0144] Moreover, if a flexible material is used for the cel itself, a support substrate, a filler, and a closure member, a solar battery can also be constituted on a curved surface. Thus, the solar battery which has various configuration and functions according to the purpose of use or an operating environment can be manufactured.

[0145] After the solar cell module of a super straight type carries out the laminating of the cel one by one on it with a sealing agent, lead wire, a tooth-back sealing agent for connection between cels, etc., conveying the front substrate sent out for example, from the substrate feeder on a band conveyor etc., it can put a tooth-back substrate or tooth-back covering, and can set and make a frame in the rim section.

[0146] After carrying out the laminating of the cel one by one on it on the other hand with the lead wire, the sealing agent, etc. for connection between cels, conveying the support substrate sent out from the substrate feeder on a band conveyor etc. in a substrate type case, a front cover can be put, and a frame can be set and produced in the periphery section.

[0147] The module of the structure shown in drawing 4 so that it may be arranged on a support substrate at that a transparent electrode, a sensitization layer, a charge transfer layer, a rear-face electrode, etc. are three-dimensional and fixed spacing Semi-conductor process techniques, such as selective plating, selective etching, and CVD-PVD, Or pattern spreading Or after applying by double width, patterning can be carried out by approaches, such as the mechanical technique, such as laser scribing, and Plasma CVM (it indicates in Solar Energy Materials and Solar Cells, 48, and p373-381 grade) or grinding. Desired module structure can be acquired by these.

[0148] Other members and processes are explained in full detail below. As a closure ingredient, liquefied EVA (ethylene vinyl acetate), liquefied EVA of the shape of a vinylidene fluoride copolymer and an acrylic resin mixture film, etc. of various materials are usable according to the purposes, such as improvement in effectiveness weatherproof grant and electric insulation grant / condensing, and improvement in cel protection nature (shock resistance).

[0149] These are doubled with the physical properties of a sealing agent as an approach of fixing on a cel, and there is an approach with various roll coats, bar coats, spray coats, screen-stencil, etc. with the ingredient of the shape of roll pressurization afterbaking adhesion, vacuum pressurization afterbaking adhesion, liquid, or a paste for a film-like material.

[0150] Moreover, a transparency filler is mixed in a sealing agent, reinforcement can be raised or light transmittance can be gathered.

[0151] It is good between a module rim and the frame surrounding a periphery for weatherability and dampproofing to close using high resin.

[0152] When using flexible materials, such as PET-PEN, as a support substrate, after letting out a roll-like base material and constituting a cel on it, the laminating of the closure layer can be continuously carried out by the above-mentioned approach, and the process that productivity is high can be built.

[0153] In order to gather generating efficiency, acid-resisting processing is performed to the front face of the substrate by the side of optical incorporation of a module (generally tempered glass). There are the approach of laminating the antireflection film and the approach of coating an acid-resisting layer in this.

[0154] Moreover, it is possible by processing the front face of a cel by the approach of grooving or a texture ring to raise the use effectiveness of the light which carried out incidence.

[0155] incorporating light in a module without a loss [****], in order to gather generating efficiency -- the maximum -- important -- it is also important to reflect the light which penetrated the photo-electric-conversion layer and reached to the inside but, and to return to a photo-electric-conversion layer side efficiently. for this reason -- being alike -- after carrying out mirror polishing of the support substrate side, there is the approach of vapor-depositing or plating Ag, aluminum, etc., a method of preparing alloy layers, such as aluminum-Mg or aluminum-Ti, in the lowest layer of a cel as a reflecting layer, or the approach of making texture structure in the lowest layer and raising a reflection factor to it by annealing treatment.

[0156] In order to gather generating efficiency, it is important to make cel connection resistance small in the semantics which suppresses an internal voltage drop.

[0157] Although it is common to connect with wire bonding or a conductive flexible sheet, the approach of carrying out pattern spreading etc. is in the location of a request of the approach and the conductive hot melt which serve as the fixed function of a cel, and an electric connect function using conductive adhesive tape or electroconductive glue.

[0158] In the solar battery using flexible base materials, such as a polymer film, by the approach shown by explanation of painting of a semi-conductor while sending out the roll-like base material, one by one, after cutting a cel in the size of formation and a request, the seal of the periphery section is carried out for the material which is flexible and has dampproofing, and a cell proper can be produced. Moreover, it can also consider as the module structure called "SCAF" of Solar Energy Materials and Solar Cells, 48, and p383 -391 publication.

[0159] In the solar battery of a flexible base material, this can also be further used for curved-surface glass etc., carrying out adhesion immobilization.

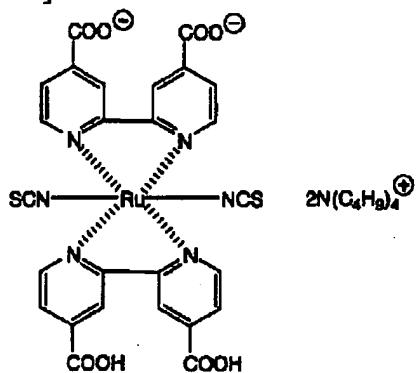
[0160]

[Example] Hereafter, the example which shows this invention with the example of a comparison explains concretely. The coloring matter and the electrolyte which were used in the example and the example of a comparison are as being shown below.

[0161]

[Formula 32]

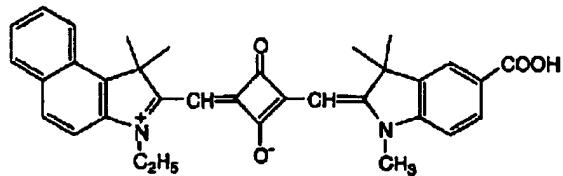
色素-1



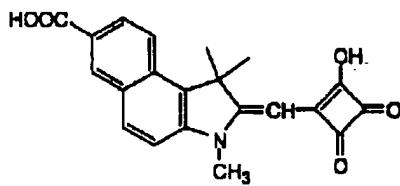
[0162]

[Formula 33]

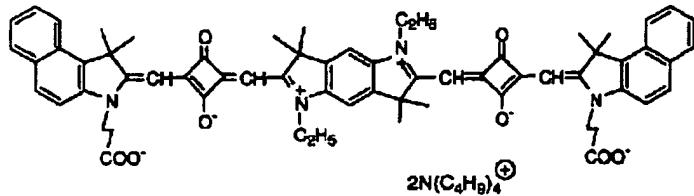
色素-2



色素-3



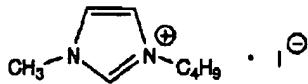
色素-4



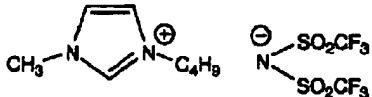
[0163]

[Formula 34]

電解質-1



電解質-2



[0164] [Example 1]

1. It is BARUBE's and others journal OBU American ceramic society except having made preparation autoclave temperature of titanium-dioxide particle content coating liquid into 230 degrees C. The titanium-dioxide distribution object of 11 % of the weight of titanium-dioxide concentration was obtained by the approach given in 80-volume 3157 page, and the same approach. The average size of the obtained titanium-dioxide particle was about 10nm. To the titanium dioxide, 30% of the weight of the polyethylene glycol (molecular weight 20,000, Wako Pure Chem make) was added in this distributed object, it mixed in it, and coating liquid was obtained.

[0165] 2. 120g of 2% of CMC water solutions and 150ml of water were added to 18g of alumina powder with a preparation mean particle diameter [of alumina particle content coating liquid] of about 0.8micro, it stirred for 3 minutes 1000 rpm using the homogenizer, and dispersion liquid were obtained. 1ml of 2% liquid of nonyl phenyl ether was added to this, and it considered as coating liquid.

[0166] 3. Apply the titanium-dioxide dispersion liquid of above-mentioned 1. to the electric conduction side side of the transparent conductive glass (the Nippon Sheet Glass make and surface electrical resistance are about 10ohm/***) which coated the tin oxide which doped the creation fluorine of the titanium-dioxide electrode which adsorbed coloring matter by the thickness of 100 micrometers with a doctor blade, and it is 25 micrometers about the alumina distribution object of above-mentioned 2. on this further after desiccation. It applied to thickness. After drying for 30 minutes at 5 degrees C, it calcinated for 30 minutes at 450 degrees C with the electric furnace (muffle furnace FP-32 made from the Yamato science mold). The thickness of the titanium-dioxide film is about 9 micrometers. The thickness of an alumina layer was about 2micro.

[0167] After taking out glass and cooling, it was immersed in the solution (3xten - four mols [l.] coloring matter, a solvent: 2-propanol) of coloring matter -1 for 18 hours. The glass which coloring matter dyed was washed by ethanol, and was made to season naturally in a dark place. The amount of adsorption of coloring matter is 2 a spreading area of 1m of a titanium dioxide. It was about 1.35xten - three mols of hits.

[0168] 4. TiO_2 which is creation **** of photoelectrochemical cell, and was made and created and by which color sensitizing was carried out The electrode substrate (2cmx2cm) was piled up with the platinum vacuum evaporationo glass of the same magnitude as this (refer to drawing 1). Next, the electrolytic solution (iodation tetrabutylammonium 0.65mol/l., acetonitrile solution of 0.05 mols/l. of iodine) is infiltrated into the clearance between both glass using capillarity, and it is TiO_2 . The photoelectrochemical cell A was obtained by introducing into an electrode. Moreover, the same photoelectrochemical cell as the above was produced as an example of a comparison except not applying an alumina distribution object. It produced photoelectrochemical cells A and B at a time by the five respectively same approaches (Table 1). as this example having shown to drawing 1 -- electrically conductive glass 1 (that by which the electric conduction agent layer 2 was ****(ed) on glass), and coloring matter adsorption TiO_2 two-layer -- the photoelectrochemical cell by which carried out the laminating of 3, the spacer layer 4, the electrolytic solution 5, the platinum layer 6, and the glass 7 to order, and the closure was carried out with epoxy system encapsulant was produced.

[0169] 5. the light of the xenon lamp of measurement 500W of photoelectric conversion efficiency (USHIO make) -- a spectrum -- simulation sunlight was generated by letting a filter (AM1.5 made from Oriel) pass. this luminous intensity -- 100 mW/cm² it was .

[0170] The electrical and electric equipment which connected the crocodile clip, respectively, irradiated simulation sunlight, and was generated on the above-mentioned electrically conductive glass and the platinum vacuum evaporationo glass of a photoelectrochemical cell was measured with the current potential measuring device (case rhe SMU238 mold). The open circuit voltage (Voc) of the photoelectrochemical cell called for by this, a short-circuit current consistency (Jsc), a form factor (FF), and conversion efficiency (eta) were collectively indicated to Table 1.

[0171]

[Table 1]

表1

| 電池 | サンプルNo. | J _{sc} (mA/cm ²) | V _{oc} (V) | FF | η(%) |
|------------|---------|---------------------------------------|---------------------|------|------|
| A (本発明) | 1 | 13.1 | 0.71 | 0.73 | 5.7 |
| | 2 | 12.7 | 0.72 | 0.72 | 5.5 |
| | 3 | 12.8 | 0.71 | 0.73 | 5.6 |
| | 4 | 13.0 | 0.71 | 0.72 | 5.6 |
| | 5 | 13.2 | 0.70 | 0.72 | 5.6 |
| B (比較例) | 1 | 12.8 | 0.69 | 0.55 | 4.1 |
| | 2 | 13.0 | 0.70 | 0.48 | 3.7 |
| | 3 | 12.9 | 0.71 | 0.69 | 5.3 |
| | 4 | 13.0 | 0.71 | 0.60 | 4.6 |
| | 5 | 12.8 | 0.70 | 0.53 | 4.0 |

[0172] By the cell which installed the spacer layer which becomes this invention from the result of the above-mentioned example in the example of a comparison to a thing with the high frequency which can do a cell with low FF, it turns out that the fixed engine performance is obtained. When resistance of the powerless component of the example of a comparison was measured, shunt resistance was low, and it turned out that the short circuit inside a cel has occurred.

[0173] [Example 2]

1. It is 5 micrometers like an example 1 on the aluminum substrate of 0.1mm thickness of 10cm four way type of production of a coloring matter adsorption electrode. The titanium-dioxide layer and alumina layer of thickness were painted, under the oxygen ambient atmosphere, it calcinated for 30 minutes at 300 degrees C, and the electrode was prepared. It left a part for an uncoated portion to the edge of a substrate by 1cm width of face for the closure and terminal ejection. Subsequently, coloring matter shown in Table 2 - The coloring matter adsorption liquid which comes to mix 2, 3 and 4, and an additive was used, and also coloring matter was made to adsorb by the approach of example 1 publication.

[0174]

[Table 2]

表2

| 成分 | 濃度 |
|------|----------------------|
| 色素-2 | 3×10 ⁻⁴ M |
| 色素-3 | " |
| 色素-4 | " |
| コール酸 | 4×10 ⁻³ M |

(溶媒: DMSO/エタノール=2.5/97.5)

[0175] 2. The sputtering technique was used for the sheet of the polyethylenenaphthalate of 50micro thickness of 10cm four way type of production of a counter electrode, patterning of the thin line (it is 5mm spacing at 500micro width of face and 2micro thickness) of aluminum was carried out, and platinum was covered with the sputtering technique in thickness of 10nm from the top to the whole surface. The sheet resistivity of the obtained sheet was 0.2ohm/**, and average light transmittance was 80%. The heat welding material of an EVA system was installed in the periphery

section of a sheet by the thickness of 10 micrometers.

[0176] 3. after infiltrating the electrolytic solution, piling up with a counter electrode sheet subsequently and making it the pressurization roller of a pair let pass and stuck to the coloring matter adsorption electrode of the production above of a photoelectrochemical cell by pressure with an imprint roller, heat welding of the periphery is carried out with a heating roller -- making -- RU -- the sheet-like photoelectrochemical cell C was produced by things. Moreover, as an example of a comparison, there was no spacer layer of an alumina, and also the photoelectrochemical cell D as well as a photoelectrochemical cell C was produced. It also produced these [five] at a time, respectively.

[0177] 4. photoelectric conversion efficiency was measured for the measurement profit **** cell of photoelectric conversion efficiency with the same measuring device as an example 1 under fine sunlight. About each cell, the result of having carried out the performance evaluation was shown in Table 3.

[0178]

[Table 3]

表3

| 電池 | サンプルNo. | J sc (mA/cm ²) | Voc (V) | F F | η (%) |
|------------|---------|----------------------------|---------|-------|-------|
| C (本発明) | 1 | 8. 5 | 0. 69 | 0. 73 | 4. 2 |
| | 2 | 7. 9 | 0. 70 | 0. 72 | 3. 9 |
| | 3 | 8. 1 | 0. 70 | 0. 73 | 4. 1 |
| | 4 | 8. 3 | 0. 71 | 0. 72 | 4. 2 |
| | 5 | 8. 5 | 0. 69 | 0. 72 | 4. 1 |
| D (比較例) | 1 | 7. 5 | 0. 69 | 0. 45 | 2. 3 |
| | 2 | 6. 8 | 0. 68 | 0. 46 | 2. 1 |
| | 3 | 7. 2 | 0. 66 | 0. 38 | 1. 8 |
| | 4 | 6. 9 | 0. 69 | 0. 44 | 2. 1 |
| | 5 | 7. 1 | 0. 68 | 0. 61 | 2. 9 |

[0179] As Table 3 shows, in the example of a comparison, it turns out that the cell of the predetermined engine performance can produce to stability by this invention to a thing with the high frequency which can do the cell of the very low engine performance.

[0180] It is 2.5 micrometers like the [example 3] operation 1. The titanium-dioxide film of thickness was produced, and the liquid which distributed the powder (mean particle diameter of about 0.5micro) of the low melting glass which consists of the presentation ratio of Pb/B/P=0.2:0.4:0.4 instead of an alumina as a spacer layer on it like the alumina of an example 1 was painted and sintered. Subsequently, coloring matter was made to adsorb like an example 1. 2microl of the electrolytic solution which becomes the obtained electrode from the ordinary temperature fused salt of a presentation of Table 4 was extended, and the electrolytic solution was made to permeate completely in an electrode by subsequently leaving it for 30 minutes under reduced pressure. Then, the same counter electrode as an example 1 was piled up.

[0181] It is 1kg/cm² from the cell E fixed in the condition that you made it pile each other up, and the exterior. The cell F which the coloring matter adsorption electrode and the counter electrode were made to approach by putting a pressure until it touched mutually was produced. Moreover, except that there was no spacer layer as an object for a comparison, the same cells G and H were produced. It produced three cell E-H at a time, respectively.

[0182]

[Table 4]

表4

| 成分 | 重量 | |
|-------|-----|---|
| 電解質-1 | 5 | g |
| 電解質-2 | 5 | g |
| ヨウ素 | 0.3 | g |

[0183] The result of having carried out the performance evaluation of the obtained cell by the same approach as an example 1 was shown in Table 5. By the cell G for a comparison, a short-circuit current is small. By the cell H which reduced an inter-electrode distance, although the increment in a short-circuit current can be attained, a fill factor serves as still lower level, and conversion efficiency does not improve. On the other hand, the spacer layer which becomes this invention is installed, an increment and fill factor of a short-circuit current increase by the cell F which made inter-electrode distance min, and it turns out that the steep increment in conversion efficiency can be attained.

[0184] That is, it turns out that the spacer layer of effectiveness of this invention is pinched and the effectiveness is demonstrated especially in the gestalt which a semi-conductor particle electrode and a counter electrode touch.

[0185]

[Table 5]

表5

| 電池 | サンプルNo. | J _{sc} (mA/cm ²) | V _{oc} (V) | FF | η (%) |
|------------|---------|---------------------------------------|---------------------|------|-------|
| E (本発明) | 1 | 6.5 | 0.60 | 0.56 | 3.5 |
| | 2 | 6.6 | 0.62 | 0.55 | 3.6 |
| | 3 | 6.7 | 0.63 | 0.57 | 3.9 |
| F (本発明) | 1 | 10.0 | 0.63 | 0.70 | 7.1 |
| | 2 | 9.5 | 0.62 | 0.71 | 6.7 |
| | 3 | 9.3 | 0.61 | 0.72 | 6.5 |
| G (比較例) | 1 | 6.4 | 0.60 | 0.50 | 3.1 |
| | 2 | 6.6 | 0.62 | 0.55 | 3.6 |
| | 3 | 6.6 | 0.61 | 0.54 | 3.5 |
| H (比較例) | 1 | 9.2 | 0.60 | 0.43 | 3.8 |
| | 2 | 9.3 | 0.60 | 0.50 | 4.5 |
| | 3 | 8.8 | 0.61 | 0.40 | 3.4 |

[0186]

[Effect of the Invention] The coloring matter sensitization optoelectric transducer and photoelectrochemical cell of the high performance which does not cause the performance degradation by the internal short circuit by this invention are obtained.

[Translation done.]